A-282

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ENGINEERING EXPERIMENT STATION

ATLANTA, GEORGIA

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Auth: Lt. AIR-2021:DB/98 to Aug '66

January 30, 1957

Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D. C.

Attention: Dr. T. L. Brownyard, Re2c

Subject: Progress Report No. 1, Project A-282, Contract NOrd-17063
Physical Organic Chemistry of Certain Nitrogen Containing Substituents
November 1, 1956 - January 28, 1957

Dear Sir:

Dr. William C. Bailey has been secured as Research Associate on the project. He began work on November 1, 1956. After reviewing the recent classified and unclassified literature in relation to our research proposal, it seems best to initiate work by determining polar substituent constants for polynitro groups and other groups of the type mentioned in the proposal. For this purpose the most useful method appears to be the kinetic study of the reactions of suitably substituted acids with diphenyldiazomethane. Therefore, preparations have been made for running kinetics on reactions of this type at 30°C. in ethanol.

So far we have determined the following rate constants:

Acid	k (l./mole-sec)
benzoic	1.02
4,4,4-trinitrobutyric	3.76
4,4-dinitrovaleric	2.03
4,4-dinitrohexanoic	2.17

The first of these values is in reasonable agreement with the average figure (1.06 reported by Roberts and co-workers, J. Am. Chem. Soc., 72, 4869 (1950); 73, 760 (1951)). Each of the rate constants given is the average value from at least three runs whose internal agreement shows that the experimental method is satisfactorily reproducible.

Following the suggestion in Dr. D. V. Sickman's letter of October 9, 1956 we plan to study trans-3-substituted acrylic acids, which have been reported to follow the Hammett equation (M. Charton, Abstracts of Papers Presented at the Atlantic City, New Jersey meeting, September 16-21, 1956, p. 83-O).

Respectfully Submitted:

Approved:

Jack Hine
Project Director

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Wyatt C. Whitley, Chief
Chemical Sciences Division

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May 2, 1957

Auth: Ltr AIR-6021:DB/98
10 Aug '66

Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D. C.

Attention: Dr. T. L. Brownyard, Re2c

Subject: Quarterly Report No. 1, Project No. A-282, Contract NOrd-17063
Physical Organic Chemistry of Certain Nitrogen-Containing Substituents
February 1 - April 30, 1957

Dear Sir:

During the period of this report the preparation of some suitably substituted trans-acrylic acids has been accomplished. These acids were purified extensively and the second-order rate constant of the reaction of each with diphenyldiazomethane determined in absolute ethanol at 30° C. Table I gives the average values of the rate constants obtained in kinetic runs of widely varying acid and diphenyldiazomethane concentrations. Also determined were the second-order rate constants for crotonic acid and acrylic acid.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR REACTION
WITH DIPHENYLDIAZOMETHANE IN ETHANOL AT 30° C

Trans Acid	k (l./mole-min)
β-acetyl-acrylic acid	4.03
β-chloro-acrylic acid	1.95
2,2,2-trichloro-crotonic acid	5.39
2,2-dichloro-crotonic acid	2.36
Acrylic acid	1.27
Crotonic acid	0.610

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When the logs of the rates for these trans 3-x-acrylic acids are plotted against the Hammett sigma constants for the para x's, a reasonable fit to a straight line is obtained. We therefore hope, by running various nitro and polynitro derivatives during the next quarter, to obtain sigma constants for the nitro-containing groups.

Attempts to prepare trans-β-methoxy-acrylic acid and γ-chloro-crotonic acid via the routes indicated below were not successful.

trans-β-Methoxy-acrylic acid.

Bromination of methyl acrylate was effected to obtain methyl α,β-dibromo-propionate; treatment of this ester with 20 per cent aqueous hydrobromic acid gave the corresponding free acid. Upon treatment of α,β-dibromopropionic acid with methanolic sodium methoxide, none of the desired trans-β-methoxy-acrylic acid was obtained. This latter reaction is reported[1] to yield ca 10 per cent of the desired product.

γ-Chloro-crotonic acid.

Ethyl vinyl-glycolate was prepared[2] by treatment of acrolein with sodium cyanide in acetic acid to obtain the corresponding cyanohydrin; treatment of this product with ethanolic hydrogen chloride followed by the addition of the calculated amount of water afforded the desired ethyl vinyl-glycolate. It is reported[3] that treatment of this hydroxy-ester with phosphorous tribromide in pyridine solution gives the rearranged product, ethyl γ-bromo-crotonate. This ester has been hydrolyzed to the corresponding free acid using barium hydroxide.[4]

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[1] Owen, L. N. and Somade, H. M. B., J. Chem. Soc., 1031 (1947).

[2] Glattfield, J. W. E. and Hoen, R. E., J. Am. Chem. Soc. 57, 1406 (1935). Glattfield, J. W. E. and Lee, E. C., J. Am. Chem. Soc. 62, 355 (1940).

[3] Ibid.

[4] Braun, G., J. Am. Chem. Soc. 52, 3167 (1930).

Analogous reaction of ethyl vinyl-glycolate with phosphorous trichloride in pyridine solution could not be effected in this laboratory. Further attempts to prepare the desired γ-chloro-crotonic acid by reacting ethyl vinyl-glycolate with thionyl chloride in pyridine solution, or treatment of the ester with either hydrogen chloride in anhydrous ethyl ether or with hydrochloric acid, followed by treatment with aqueous barium hydroxide,[1] did not give the desired product.

Further attempts to prepare these two acids are in progress.

Respectfully submitted:

Jack Hine
Project Director

Approved:

Wyatt C. Whitley, Chief
Chemical Sciences Division

[1] Braun, G., J. Am. Chem. Soc., 52, 3167 (1930).

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August 9, 1957

Auth: Ltr AIR-6021:DB/98
20 Aug '62

Chief, Bureau of Ordnance
Department of the Navy
Washington 25, D. C.

Attention: Dr. T. L. Brownyard, Re2c

Subject: Quarterly Report No. 3, Project No. A-282, Contract NOrd-17063
Physical Organic Chemistry of Certain Nitro-Containing Substituents
May 1, 1957 to July 31, 1957

Dear Sir:

During the period of this report the second-order rate constants for the reaction between various suitably substituted acrylic acids and diphenyldiazomethane have been determined in absolute ethanol at 30° C. Table I gives the average values of the rate constants obtained in kinetic runs of widely varying acid and diphenyldiazomethane concentrations.

TABLE I

SECOND-ORDER RATE CONSTANTS FOR REACTION
WITH DIPHENYLDIAZOMETHANE IN EHTANOL AT 30° C

Trans Acid	k (l./mole-min)
β-nitroacrylic acid	21.83
4,4-dinitropentenoic acid	11.50
4,4-dinitrohexenoic acid	13.00
4-methyl-4-nitropentenoic acid (trans)	2.49
4-methyl-4-nitropentenoic acid (cis)	3.47

Further attempts to prepare β-methoxyacrylic acid and γ-chlorocrotonic acid via the routes indicated below have been made. Although these acids have not

been obtained in a pure state, indications at present suggest that they may be obtained in the near future.

trans-β-methoxyacrylic acid

This preparation was described in a report from this laboratory dated May 2, 1957. Two further attempts to obtain this acid have afforded no crystalline material. A product, bp 108° C/5mm has been isolated, however, and attempts at further purification are in progress in order that the desired crystalline acid may be obtained.

γ-chloro-crotonic acid

Negative results have been obtained in the attempted allylic chlorination of methyl crotonate using N-chlorosuccinimide under a variety of conditions. Although N-chlorosuccinimide is not primarily a chlorinating agent, it was hoped that some of the desired chloro-ester nevertheless would be obtained. Treatment of methyl crotonate with N-chlorosuccinimide in benzene or ether with or without benzoyl peroxide catalyst at room temperature and at reflux temperature afforded none of the desired ester. In all instances, no essential reaction occurred.

Treatment of methyl crotonate with N-bromosuccinimide in chloroform afforded a good yield of methyl γ-bromocrotonate. This ester was hydrolyzed to crude γ-hydroxycrotonic acid using aqueous potassium carbonate[1]. It is reported[2] that treatment of this acid with thionyl chloride affords the desired γ-chlorocrotonic acid, mp 83° C.

Attempts to prepare two unknown acids, p-isocyanobenzoic acid and p-azidobenzoic acid, have been unsuccessful. Treatment of p-aminobenzoic acid with sodium hydroxide and chloroform in methyl alcohol solution[3] led to polymeric material from which no crystalline acid corresponding to p-isocyanobenzoic acid could be obtained. Treatment of p-bromobenzoic acid with silver cyanide in anhydrous ether or benzene led to no reaction at room temperature or to polymeric material at elevated temperatures.

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[Contribution from the Georgia Institute of Technology]

THE MECHANISM OF THE BASIC DECOMPOSITION OF 1,1,1,3-TETRANITRO-2-PHENYLPROPANE AND OF THE ADDITION OF NITROFORM TO β-NITROSTYRENE

By

Jack Hine and Lloyd A. Kaplan

The kinetics of the decomposition of 1,1,1,3-tetranitro-2-phenylpropane to nitroform and β-nitrostyrene have been studied in the presence of pyridine-pyridine hydrochloride buffers in absolute methanol solution. These studies show the reaction to be subject to general base catalysis. The decomposition reaction has also been studied in methanolic hydrogen chloride solutions where the basic catalyst is the solvent methanol. A mechanism is proposed in agreement with the data obtained. From this mechanism, rate constants obtained in studying the decomposition reaction, and the equilibrium constant for the reaction, a kinetic equation may be derived for the reverse reaction, the addition of nitroform to β-nitrostyrene. The kinetic data observed for the addition reaction are in fairly good agreement with this equation.

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Introduction

While qualitative observations and analogies with other more carefully studied reactions may be used to suggest quite plausible mechanisms for the Michael reaction and its reversal, as recently as 1951 no kinetic study of the reaction has been reported.[1] Since that time, Kamlet and Glover have reported a study of the kinetics of the addition of barbituric acid to various β-nitrostyrenes.[2] We should like to report a study of the decomposition of 1,1,1,3-tetranitro-2-phenylpropane (HA) and of the reverse reaction, the addition of nitroform (HNF) to β-nitrostyrene (NS).

$$C_6H_5CHCH_2NO_2(C(NO_2)_3) \rightleftharpoons C_6H_5CH{=}CHNO_2 + HC(NO_2)_3$$

HA NS HNF

Results and Discussion

Preliminary studies showed that at room temperature HA dissociated at a negligible rate in hexane, very slowly in ether, somewhat faster in dioxane, and much more rapidly in methanol. While the reaction in pure methanol was initially quite rapid, being observable within a few seconds at 25°, it became much slower as the reaction proceeded presumably because the liberated nitroform increased the acidity of the solution. This presumption was supported by the observation that in a methanol solution 0.004 N in HCl, less than 3% decomposition occurred in 19 hours at 25°. It therefore seemed likely that the reaction in pure methanol was due to catalysis by methoxide ions.

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(1) C. K. Ingold, Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, New York, 1953, Sec. 44b.
(2) M. J. Kamlet and D. J. Glover, Abstracts of Papers, 127th ACS meeting, Cincinnati, Ohio, March 29-April 7, 1955, p. 35N.

To facilitate kinetic studies the ionization constant of nitroform (K_N) was determined spectrophotometrically in methanol at 25° and 40° at various ionic strengths with the results listed in Table I.

TABLE I

IONIZATION CONSTANTS (K_N) OF NITROFORM IN METHANOL

Ionic Strength	$K_N \times 10^4$ 25°	40°
0.5	17.6	--
0.3	11.8	--
0.2	9.41	9.39
0.1	5.92	5.86
0.04	3.61	--
0.002	1.30	--
0.000[a]	1.20[a]	--

[a]Extrapolated.

The Reaction in Pyridine Buffers.--In order to learn whether the reaction was general or specific base catalyzed kinetic studies were made using pyridine-pyridine hydrochloride buffers. Under these conditions the reaction proceeds essentially completely to products. The reaction was followed by spectrophotometric measurements since β-nitrostyrene and the nitroform anion absorb strongly at wavelengths between 3000 and 4000 Å while the reactant, HA, does not. When the concentration of HA was small compared to that of the buffer, so that the nitroform liberated during the reaction did not appreciably change the buffer ratio, good first order rate constants were obtained. For data on a typical run see Table VI. The rate constants obtained at several buffer ratios and concentrations at 25° and 38° are listed in Table II.

TABLE II

RATE CONSTANTS FOR THE DECOMPOSITION OF HA IN METHANOLIC PYRIDINE BUFFERS[a]

Temp. (°C)	10^3 [C_5H_5N]	10^3 [$C_5H_5NH^+$]	$10^5 k$ (sec^{-1})
25.0	4.141	4.147	3.58 ±0.02[b]
25.0	2.455	1.228	2.40 ±0.12
25.0	4.910	2.456	4.68 ±0.10
25.0	9.076	3.025	7.67 ±0.05
25.0	18.15	6.050	15.35 ±0.47
38.0	2.046	0.682	5.18 ±0.13
38.0	3.758	1.698	8.97 ±0.14
38.0	4.163	1.387	9.53 ±0.05

[a]Sodium perchlorate added to keep the ionic strength at 0.1 in all cases.
[b]Average deviation.

From these rate constants it may be seen that the reaction is general base catalyzed and that most of the reaction is due to pyridine catalysis under the conditions employed. The most resonable reaction mechanism appears to be

(I) $$HA + MeO^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A^- + MeOH$$

$$HA + C_5H_5N \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} A^- + C_5H_5NH^+$$

$$HA + MeOH \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} A^- + MeOH_2^+$$

$$HA + NF^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} A^- + HNF$$

$$A^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} NS + NF^-$$

where A^- is $C_6H_5\overset{\ominus}{C}HCHNO_2$ with $C(NO_2)_3$ on the CH,

and k_{-1} and k_3 will be treated as first order rate constants. At this point the symbols for the ionization constant of pyridine

$$K_P = \frac{[C_6H_5NH^+][MeO^-]}{[C_5H_5N]}$$

the autoprotolysis constant of methanol

$$K_M = [MeOH_2^+][MeO^-]$$

the ionization constant of HA

$$K_{HA} = \frac{[MeOH_2^+][A^-]}{[HA]}$$

and the equilibrium constant for the decomposition of HA

$$K_E = \frac{[NS][HNF]}{[HA]}$$

may also be introduced. From the steady state treatment of that part of the reaction due to pyridine the

$$v = \frac{k_2k_5\,[C_5H_5N][HA]}{k_{-2}\,[C_5H_5NH^+] + k_5} .$$

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Thus, the first order rate constants for the reaction of HA could be represented

$$k = \frac{k_2\,[C_5H_5N]}{(k_{-2}/k_5)[C_5H_5NH^+] + 1} \qquad (1)$$

if all of the reaction were due to pyridine.

The observation of general base catalysis shows that k_5 may not be neglected in comparison to $k_{-2}[C_5H_5NH^+]$.

Assuming catalysis by the bases methanol and methoxide ion to be negligible and neglecting $k_{-2}[C_5H_5NH^+]$ in comparison to k_5, a least squares calculation gives values of k_2 whose predictions of k are in error by an average 5%. Since the average percentage of deviation in the experimental determination of the rate constants was about 2% it seems quite probable that this lack of strict proportionality between pyridine concentration and reaction rate requires an explanation. Each of three specific versions of mechanism I appears to give such an explanation.

Mechanism Ia suggests that catalysis by bases other than pyridine is negligible under the conditions used, but that $k_{-2}[C_5H_5NH^+]$ may not be neglected in comparison to k_5. Thus with the values: $k_2^{25°} = 0.0101$, $k_2^{38°} = 0.0252$, and $k_{-2}/k_5 = 40$, the first order rate constants of Table II may be calculated with an average deviation of about 3%.

Mechanism Ib hypothesizes that $k_{-2}[C_5H_5NH^+]$ is negligible compared to k_5, but that some of the reaction is due to catalysis by methoxide ions. It may be shown that

$$\frac{k_2\,[C_5H_5N]}{k_1\,[MeO^-]} = \frac{k_{-2}\,[C_5H_5NH^+]}{k_{-1}} \qquad (2)$$

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Therefore, if most of the reaction is due to pyridine as in the present case, k_{-1} must be smaller than $k_{-2}[C_5H_5NH^+]$ and hence negligible compared to k_5. Thus, the first order rate constant would be represented

$$k = k_1 [MeO^-] + k_2 [C_5H_5N]. \qquad (3)$$

Using K_P, values of k_1 and k_2 were calculated by a least squares method, the percent deviations from the experimental being minimized.[3] These values, $k_1^{25°} = 5.68 \times 10^4$, $k_1^{38°} = 5.81 \times 10^4$, $k_2^{25°} = 8.105 \times 10^{-5}$, and $k_2^{38°} = 21.96 \times 10^{-3}$ (all in l./mole^{-1} sec^{-1}) reproduced the k's in Table II with an average deviation of about 2%.[4]

Mechanism Ic also involves the assumption that $k_{-2}[C_5H_5NH^+]$ is negligible compared to k_5 and further assumes catalysis by the base methanol while neglecting any methoxide ion catalysis. Since an equation of the type of (2) may be used to show that with these assumptions $k_{-3}[MeOH_2^+]$ may be neglected in comparison to k_5 under the reaction conditions employed, it may be seen that

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(3) K_P was calculated from the acidity constant (pK 5.55) of the pyridinium ion [H. Goldschmidt and E. Mathieson, Z physik. Chem., 119, 439 (1926) and $K_M^{25°}$ (pK_M 16.66) N. Bjerrum, A. Unmack, and L. Zechmeister, Kgl. Danske Videnskab, Math. fys. Medd., 5, No. 11 (1925); Chem Abstr., 19, 3196 (1925)]. The value of pK_M was corrected to 15.97 for $\mu = 0.1$ by the assumption that changing ionic strength has the same effect as observed on pK_N. (See Table I.) Since no temperature coefficient was available for the acidity constant of the pyridinium ion, the same pK_P (10.42) was used at both temperatures.

(4) While the assumption that K_P has the same value at 38° as at 25° can have no effect on the ability (or inability) of equation (3) to fit the experimental data, it does affect the magnitude of $k_1^{38°}$ obtained. If $K_P^{38°}$ is smaller than $K_P^{25°}$ the value of $k_1^{38°}$ will be larger than that listed. The ionization constants of some amines increase with increasing temperature, while others decrease. E.g., see the data of D. H. Everett and W. F. K. Wynne-Jones, Proc. Roy. Soc. (London), A177, 499 (1941).

$$k = k_2 [C_5H_5N] + k_3. \qquad (4)$$

A least squares treatment gives the values $k_2^{25°} = 0.00819$, $k_2^{38°} = 0.02117$, $k_3^{25°} = 3.7 \times 10^{-6}$, and $k_3^{38°} = 8.6 \times 10^{-6}$ capable of reproducing the rate constants of Table II with an average deviation of about 2.5%.

The Reaction in Methanolic HCl.--Since mechanisms Ia, b, and c do not differ significantly in their agreement with the data shown in Table II, additional experimental evidence was obtained by making kinetic studies on the decomposition reaction in the presence of various concentrations of HCl at 40°. The first order rate constants obtained are listed in Table III. The rate is

TABLE III

RATES OF DECOMPOSITION OF HA IN METHANOLIC HCl AT 40°

[HCl]	$k \times 10^7$ sec^{-1}
0.0903[a]	6.28 ±0.14
0.0221[b]	9.53 ±0.19
0.0048[b]	11.69 ±0.39

[a]Ionic strength 0.0903.
[b]Sodium perchlorate added to bring ionic strength to 0.10.

seen to continue to fall with increasing acidity throughout the range studied. It might be suggested that this decrease is due to the decreasing methoxide ion concentration, with the first order rate constant following the equation

$$k = k_1 [MeO^-] + k_3.$$

The optimum values calculated by a least squares method to fit the data in Table III are $k_1^{40°} = 5.65 \times 10^6$ and $k_3^{40°} = 6.60 \times 10^{-7}$. However, these values

give an average deviation of more than 10% in predicting the rate constants in Table III. Furthermore, the value of $k_1^{40°}$ required is more than 100 times as large as the $k_1^{38°}$ calculated on the assumption that mechanism Ib operates in pyridine buffer. If mechanism Ia and I or Ic operate in addition to or instead of Ib the calculated $k_1^{38°}$ would be even smaller. It, therefore, seems unlikely that methoxide catalysis is significant in the runs described in Table III.

A more reasonable explanation for the decrease in rate is the assumption that under the more acidic conditions used in these runs an appreciable fraction of the intermediate A^- ions formed is reconverted to HA. In other words

$$k = \frac{k_3}{r_3 [MeOH_2^+] + 1} \qquad (5)$$

where $r_3 = k_{-3}/k_5$.

With the values $k_3^{40°} = 1.194 \times 10^{-6}$ and $r_3^{40°} = 10$, Eq. (5) reproduces the rate constants of Table III with an average deviation of 1.8%.

Since

$$\frac{k_3}{k_2 [C_5H_5N]} = \frac{k_{-3} [MeOH_2^+]}{k_{-2} [C_5H_5NH^+]}$$

$$\frac{k_{-2}}{k_5} = \frac{r_3 k_2 K_M}{k_3 K_P} \quad .$$

From this relationship and the values of K_M and K_P used previously[3] k_{-2}/k_5 may be calculated to be 2.5 in contrast to the value of about 40 required by the exclusive operation of mechanism Ia for the reaction in the presence of

pyridine buffers. Although this value of k_{-2}/k_5 is subjected to the errors present in K_N and K_P we believe there is another strong argument against mechanism Ia. Namely the value of 40 for k_{-2}/k_5 would make k_{-2}, the rate constant for the donation of a proton from pyridinium ion to the base A^-, four times as large as k_{-3}, the rate constant for the donation of a proton from the methyloxonium ion to the same base.

The fact that mechanism Ic requires values of $k_3^{25°}$ and $k_3^{38°}$ much larger than the $k_3^{40°}$ determined more directly from the data of Table III shows that catalysis by the base methanol is very slight in the pyridine buffer reaction.

The Addition of HNF to NS.--In order to provide information about the reverse reaction, the addition of nitroform to β-nitrostyrene, the equilibrium constant (K_E) was determined. The method of approach from both sides as illustrated in Fig. 1 gave

$$\log K_E^{40°} = -1.20 \pm 0.03 \text{ or } K_E^{40°} = 0.063 \pm 0.004 .$$

From the study of the decomposition reaction, it is clear that at hydrogen ion concentrations greater than about 0.001, k_1 and k_{-1} may be neglected. According to the principle of microscopic reversibility, this must be true for the addition reaction too.

The establishment of K_E permits a determination of the value of an additional rate constant, k_{-5}, since

$$\frac{k_3 k_5}{k_{-3} k_{-5}} = \frac{[NS][MeOH_2^+][NF^-]}{[HA]}$$

$$k_{-5} = \frac{k_3}{r_3 K_E K_N} = 3.23 \times 10^{-3} .$$

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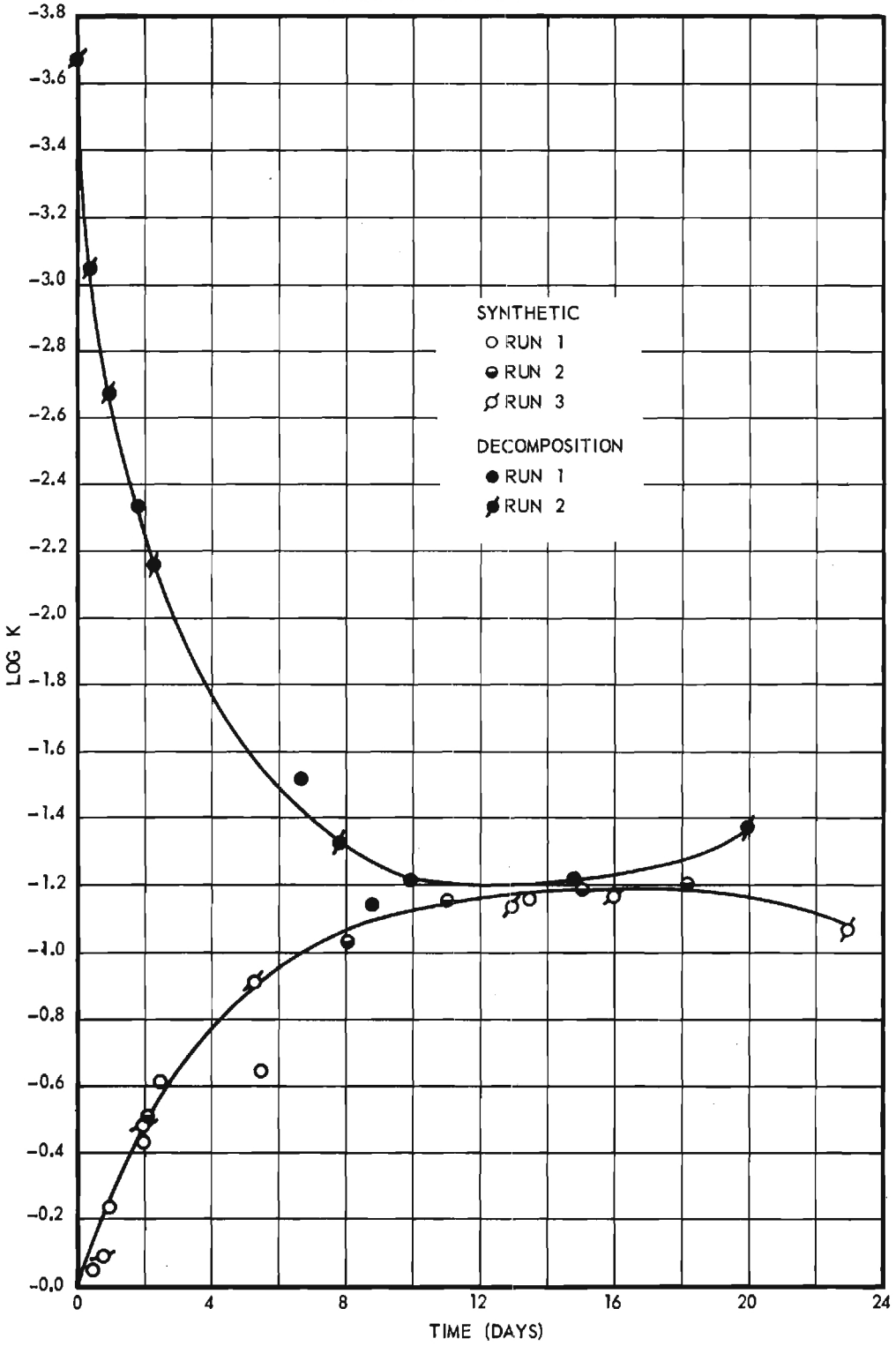

Figure 1. Plot of Log K_E Versus Time at 40°.

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The next measurements made were on the kinetics of the addition of HNF to NS. If mechanism I operates for the decomposition reaction it must, of course, also operate (in reverse) for the addition reaction. In the decomposition reactions, the concentrations of HNF and NF^- never reached any significant level (the reactions were run in quite dilute solutions) so that the terms involving k_4 and k_{-4} could always be neglected. In order to get the addition reaction to proceed to an appreciable extent, however, it is necessary to use relatively high concentrations of nitroform. While these higher concentrations make the solution sufficiently acidic to neglect the k_1 and k_{-1} terms, the k_4 and k_{-4} terms are considered in deriving a kinetic equation, as follows. From the steady state approximation,

$$[A^-] = \frac{k_3\,[HA] + k_4\,[HA][NF^-] + k_{-5}\,[NS][NF^-]}{k_{-3}\,[MeOH_2^+] + k_{-4}\,[HNF] + k_5} \qquad (6)$$

therefore,

$$\frac{d\,[HA]}{dt} = \frac{(r_3 k_{-5} K_N\,[NS][HNF] - k_3\,[HA])(1 + [NF^-]\,k_4/k_3)}{r_3\,[MeOH_2^+] + r_4\,[HNF] + 1} \qquad (7)$$

where $r_4 = k_{-4}/k_5$. Since the terms $[NF^-]\,k_4/k_3$, $r_3[MeOH_2^+]$, and $r_4[HNF]$ are not too large compared to one we may take the values of $[NF^-]$, $[MeOH_2^+]$, and [HNF] (in the denominator but not in the numerator) as their average values during a run. That is, in a given run we have a constant, C

$$C = \frac{1 + [NF^-]\,k_4/k_3}{r_3\,[MeOH_2^+] + r_4\,[HNF] + 1}\,.$$

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Calculations show that C never varies from its average by as much as 0.5% in our runs. If $x = [HA]$ and $a = [HNF]_o$ (this is the concentration of HNF actually present in the undissociated form, not the formal concentration) then the approximation $[HNF] = (a - x)$ is never in error by as much as 0.2% in our runs. With these approximations Eq. (7) becomes

$$\frac{dx}{dt} = C\,[A(a - x)(b - x) - k_3 x] \qquad (8)$$

where $A = r_3 k_{-5} K_N$ and $b = [NS]_o$. Integration of (8) gives

$$2.3 \log \frac{(D + B - 2Ax)(D - B)}{(D - B - 2Ax)(D + B)} = BCt$$

where $B = \sqrt{A^2(a - b)^2 + 2k_3 A(a + b) + k_3^2}$ and $D = A(a + b) + k_3$. Since terms containing k_4 and k_{-4} are found only in the constant C, a plot of the logarithmic term in Eq. (9) versus time should give a straight line whether k_{-4} and k_4 are significant or not. From the values we have already determined for r_3, k_3, k_{-5}, and K_N and the data on an individual kinetic run on the addition reaction such plots were made (see Fig. 2). The run described by solid circles was carried out at an ionic strength of only about 4×10^{-3} (due to the ionized nitroform) rather than 0.1 at which the values of r_3, k_3, k_{-5}, and K_N were determined. However, only reactions between ions should be greatly affected by the change in ionic strength. Only r_3 and K_N relate to reactions of this type and since these values will change in opposite directions the reaction rate should not change greatly with changing ionic strength. The points in Fig. 2 lie fairly near straight lines, in support of our proposed reaction mechanism. The straight lines shown, however, were not chosen to fit the data,

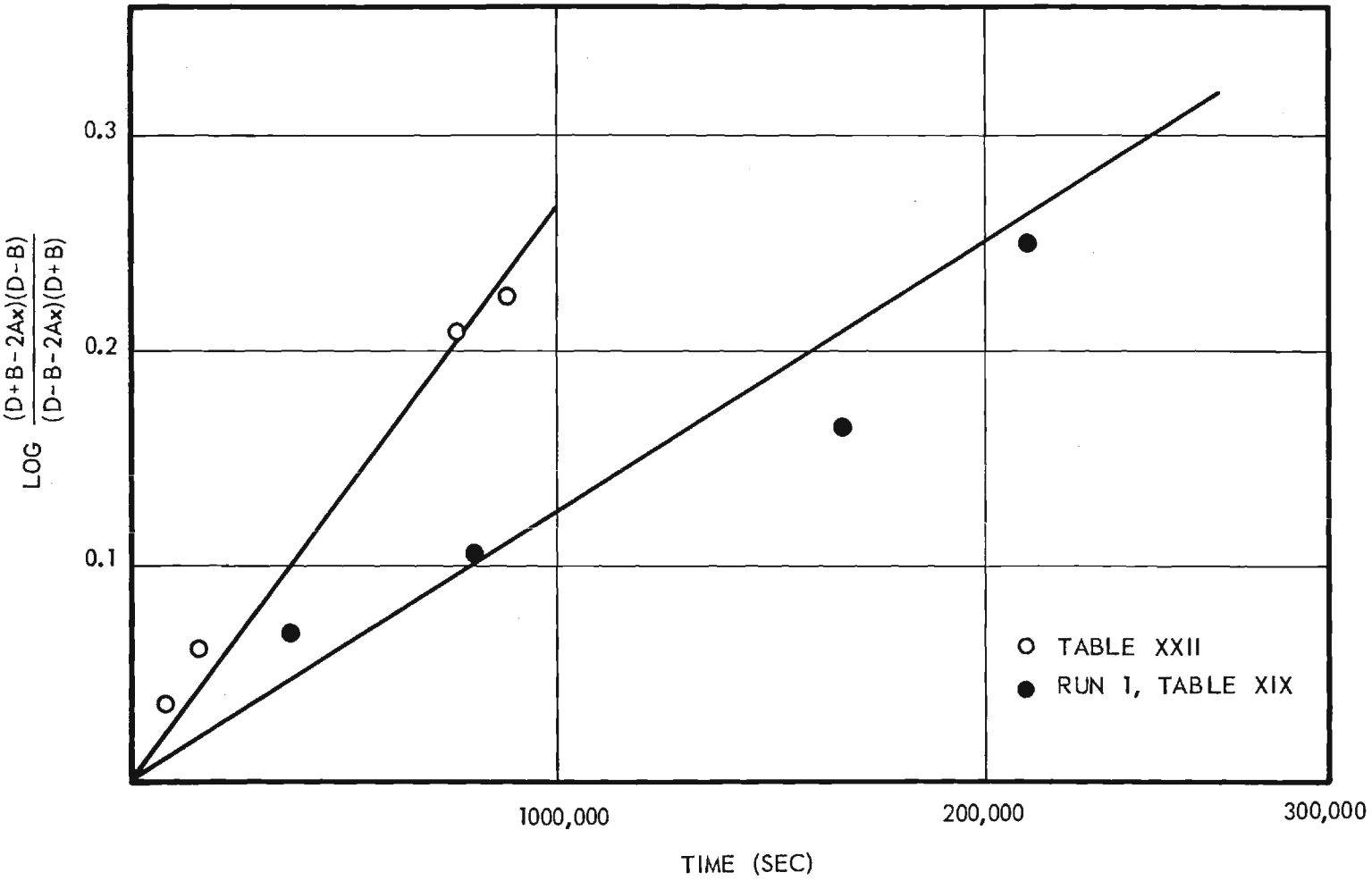

Figure 2. Kinetic Plot for Addition of Nitroform to β-Nitrostyrene.

but were calculated from Eq. (9) on the assumption that the terms $[NF^-]k_4/k_3$ and $r_4[HNF]$ were negligible. From the agreement observed it is believed that most of the reaction goes through the path governed by k_3 and k_{-3} and not more than one fifth of it through the path governed by k_4 and k_{-4}.

From the ionization constant of HA it is possible to calculate some other of the rate constants of mechanism I. The rapidity of the base catalyzed decomposition prevents a determination of this ionization constant. However, we have estimated it by the method of Branch and Calvin.[5] Using their inductive constants and as a reference compound nitroethane,[6] the pK of HA may be estimated as 3.4 in aqueous solution.

There appears to be a correlation between the extent to which the ionization constants of acids decrease upon going from water to methanol and the degree of concentration of charge in the anion of the acid. The pK's of carboxylic acids increase by about 4.9 units on the average while those of nitroform and picric acid increase by about 3.0 units.[7] We estimate that aliphatic mononitrocompounds should have pK's about 4.5 units greater in methanol than in water. We believe that the resultant estimate of the pK of HA in methanol (7.9) is reliable within one or two units.

In order to get somewhat better values of k_1 and k_2 than those calculated on the assumption of the exclusive operation of mechanism Ib for the reaction in pyridine buffers we have estimated the correction necessary for catalysis

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(5) G. E. K. Branch and M. Calvin, The Theory of Organic Chemistry, Prentice-Hall Inc., New York, 1941, chap. VI.

(6) G. W. Wheland and J. Farr, THIS JOURNAL, 65, 1433 (1943) report pK = 8.6 in water.

(7) I. M. Kolthoff, J. J. Lingane and W. D. Larson, THIS JOURNAL, 60, 2512 (1938); I. M. Kolthoff and L. S. Guss, ibid., 61, 330 (1939); L. D. Goodhue and R. M. Hixon, ibid., 56, 1329 (1934).

by the base methanol in these runs. Assuming that the activation energy for k_3 is near that for k_2 we got $k_3^{25°} = 0.04 \times 10^{-5}$ and $k_3^{38°} = 0.10 \times 10^{-5}$. We then obtained the values of k_1 and k_2 listed in Table IV from the equation

$$k = k_1 [MeO^-] + k_2 [C_5H_5N] + k_3$$

and the data in Table II, by the method of least squares.

From our estimated value of pK_{HA} we have calculated values of k_{-1}, k_{-2}, k_{-3}, and k_5 at 40° since k_2, k_3, K_N, and K_E are all known fairly reliably at this temperature. These values (Table IV) all contain the uncertainty in our estimate of K_{HA} but this does not affect their relative magnitudes.

TABLE IV

RATE CONSTANTS FOR MECHANISM I

Determined		Estimated from pK_{HA}	
$k_1^{25°}$	$\sim 5.2 \times 10^4$	$k_{-1}^{40°}$	$\sim 2 \times 10^{-3}$
$k_1^{38°}$	$\sim 5.1 \times 10^4$	$k_{-2}^{40°}$	~ 25
$k_2^{25°}$	8.097×10^{-3}	$k_{-3}^{40°}$	$\sim 10^2$
$k_2^{38°}$	2.189×10^{-2}	k_5	~ 10
$k_3^{40°}$	1.194×10^{-6}	$k_{-4}^{40°}$	< 1
$k_4^{40°}$	$< 2 \times 10^{-5}$		
k_{-5}	3.23×10^{-3}		

In addition k_1, k_{-1}, and k_{-2} are affected by inacuracies in K_P and K_M, and k_1 and k_{-1} cannot be very accurate because such a small fraction of the reaction

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in pyridine buffers is due to methoxide catalysis. For this latter reason the fact our least squares treatments gave a $k_1^{38°}$ smaller than $k_1^{25°}$ cannot be considered significant evidence against the proposed reaction mechanism.

As an independent check on mechanism I, it is useful to consider whether the magnitudes of the k's of Table IV are reasonable in view of what is known about the kinetics of related reactions. The estimates of k_4 and k_{-4} are believed to be conservative. It, therefore, appears very probable that k_{-4} is smaller than k_{-2}. I.e., although nitroform is more than 100 times as strong an acid as the pyridinium ion, it donates protons to A^- more slowly. While this may at first seem surprising, it is actually in good agreement with the generalization that acidic protons attached to carbon are donated to bases more slowly than equally acidic protons attached to oxygen or nitrofrom. Thus, the ammonium ion (pK ~ 10) undergoes deuterium exchange in acidic aqueous solution at 0°[8] millions of times more rapidly than nitroethane (pK ~ 8.6) would under these conditions.[9] It is probable that steric hindrance is also of importance in decreasing the reactivity of nitroform.

The rate constants observed for the removal of a proton from nitroethane by various bases are: $k = 1.25 \times 10^{-7}$ sec^{-1} for water,[9] $k = 3.57 \times 10^{-4}$ liters mole^{-1} sec^{-1} for pyridine,[10] $k = 8.04$ liters mole^{-1} sec^{-1} for hydroxide ions,[11] all in aqueous solution at 34.85°. Pearson and coworkers' observations that

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(8) A. I. Brodski and L. V. Sulima, Doklady Akad. Nauk S.S.S.R., 74, 513 (1950); cf. Louis Kaplan and K. E. Wilzbach, THIS JOURNAL, 76, 2593 (1954); and C. G. Swain, J. T. McKnight, M. M. Lakes, and V. P. Kreiter, ibid., 76, 4243 (1954).
(9) R. G. Pearson and R. L. Dillon, ibid., 72, 3574 (1950).
(10) R. G. Pearson and F. V. Williams, ibid., 75, 3073 (1953).
(11) Extrapolated from the data of R. P. Bell and J. C. Clunie, Proc. Roy. Soc. (London), A212, 16 (1952).

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pyridine is 2860 times as reactive as water toward nitroethane compared to our findings that pyridine is 2220 times as reactive as methanol toward HA is reasonable (even though methanol is a weaker base than water[12]) since the stronger acid HA should be less selective in its reactions. The relative magnitude of k_1 and the absolute magnitudes of all of our k's are believed to be in the general area expected, when the following factors are considered. Reactions like those governed by k_2 and k_3, in which there is charge formulation in the transition state, should proceed more rapidly in water than in methanol.[13] Reactions like those of the hydroxide and methoxide ions with nitrocompounds should be faster in methanol.[13] The methoxide ion is a slightly weaker base than the hydroxide ion.[14] Nitroethane is a weaker acid than HA.

Fig. 3 is a Brønsted type plot of our rate constants for reaction of A^- with various acids (open circles) and those calculated from the data of Pearson and Williams[10] on the reaction of the nitroethane anion with various acids. In this calculation it was assumed that the various substituted pyridine bases will react 37% faster in pure water than in 30% ethanol just as pyridine does. We have followed Pearson and Williams in drawing the best line through their data on pyridinium ions ignoring such di-orthosubstituted ions as 2,6-dimethylpyridinium and 2-methylquinolinium which react slowly because of steric hindrance. It is seen that if a line parallel to that through these workers' data were drawn through our point for the pyridinium ion that the points for

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(12) H. Goldschmidt and A. Thuesen, Z. physik. Chem., 81, 30 (1912); H. Goldschmidt and P. Dahll, ibid., 108, 121 (1924).

(13) This follows from the theory of solvent effects described by C. K. Ingold, Structure and Mechanism in Organic Chemistry. Cornell University Press, Ithaca, New York, 1953, Sec. 25. For specific supporting data see ref. (10).

(14) J. Hine and M. Hine, THIS JOURNAL, 74, 5266 (1952).

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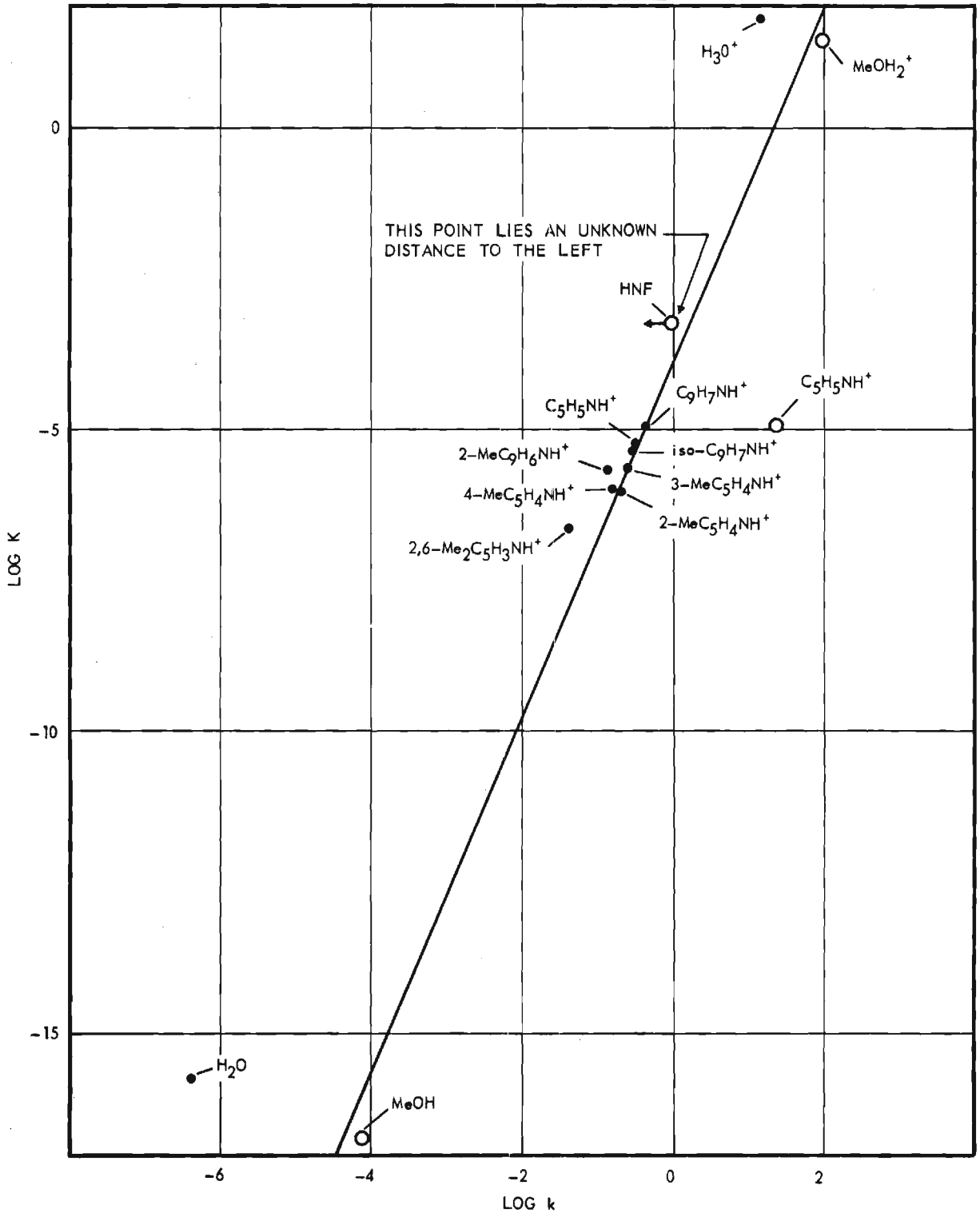

Figure 3. Bronsted-Type Plot of Logs of Acidity Constants of Acids Versus Logs of Rate Constants for Proton Donation to: ● the Nitroethane Anion; ○ A⁻.

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methyloxonium ion and methoxide ion would deviate in the same direction and to about the same extent as the points for the hydronium and hydroxide ions do for their line. We therefore believe that both the relative and absolute magnitudes of our rate constants are reasonable and that this fact supports our mechanistic interpretation.

The only rate constants determined with sufficient precision at two temperatures to warrant calculating activation parameters was k_2, for which we calculate $\Delta H^{\pm} = 13.5$ kcal/mole and $\Delta S^{\pm} = -16.8$ e.u. from the absolute rate equation[15]

$$k = \frac{kT}{h} e^{-H^{\pm}/RT} e^{S^{\pm}/R} .$$

A comparison of these data with those of Pearson and Williams[10] show that the greater reactivity of HA than nitroethane toward pyridine is partly an entropy and partly an enthalpy effect.

Other Reaction Mechanisms.--There are other reaction mechanisms such as a concerted one-step E2 type[16] elimination reaction (II)

$$\text{(II)} \quad HA + B \rightarrow NS + NF^- + BH^+ \text{ and}$$

$$\text{(III)} \quad HA + B \rightleftharpoons A^- + BH^+$$

$$A^- + BH^+ \rightarrow NS + HNF + B$$

which explain the observed base catalysis but not the data of Table III.

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(15) S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes. McGraw-Hill Book Co., New York, N. Y., 1941, p.14.

(16) C. K. Ingold, op. cit., Sec. 30a.

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Experimental

Preparation and Purification of Reagents.--Potassium nitroform was prepared from tetranitromethane by the method of Macbeth and Orr.[17] To liberate nitroform from its potassium salt, dry hydrogen chloride was passed into a stirred suspension of the salt in hexane until the original bright yellow color became a very pale yellow. Then dry nitrogen was bubbled through the mixture to remove the excess hydrogen chloride. The mixture was filtered and cooled in a dry-ice bath. The white crystalline nitroform that separated on cooling was collected on a filter with exclusion of moisture and then distilled at reduced pressure through a 9-cm Vigreaux column in an all glass still. The material collected at 48-49° (15 mm) crystallized at room temperature (25°) to a white solid that became yellow upon exposure to much atmospheric moisture. Only white material was used in these investigations. ALL OPERATIONS WITH NITROFORM AND ITS SALT WERE CARRIED OUT WITH ADEQUATE PRECAUTIONS SINCE BOTH MATERIALS ARE EXPLOSIVE.

Methanol was purified by the method of Vogel.[18] Pyridine was fractionated over potassium hydroxide. Anhydrous sodium perchlorate was prepared by crystallization from a saturated solution at a temperature above the transition temperature of 53°,[19] dried in a vacuum desiccator and found, by a Karl Fischer titration to contain about 0.045% water. The neutrality of the sodium perchlorate was shown by the fact that for a 1 M methanolic solution, the amount of base required to titrate to the bromthymol blue end point and the amount of

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(17) A. K. Macbeth and W. B. Orr, J. Chem.Soc., 534 (1932).
(18) A. I. Vogel, Textbook of Practical Organic Chemistry. 2nd ed., Longmans Green and Co., London, p. 168.
(19) E. Cornec and J. Dickely, Bull. Soc. Chim. France, [4] 41, 1017 (1923).

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acid required for the bromphenol blue end point were both the same as the amounts required for pure methanol, within the experimental error.

To prepare the 1,1,1,3-tetranitro-2-phenylpropane, 13.6 g. of nitroform was added to a solution of 8.94 g. of β-nitrostyrene in methanol. Water was added to the cloud point and the mixture was kept at 40° for 4 hours. Upon cooling and filtering 5.75 g. of white crystals was obtained and the mother liquors reheated to 40° for 4 more hours. A second cooling and filtration gave an additional 2.75 g. of product. Upon recrystallization from hexane, the combined crystals gave 7.39 g. (41%) of white needles, m.p. 87-88°.

Spectral Measurements.--By use of a Beckman model DU spectrophotometer, it was shown that the β-nitrostyrene has an absorption maximum at 3100 Å and that the nitroform anion has one at 3500 Å. The absorption of nitroform and HA was small above 3000 Å. Beer's law plots gave straight lines and the extinction coefficients shown in Table V.

TABLE V

EXTINCTION COEFFICIENTS[a]

Species	ϵ_{3100}[b]	ϵ_{3500}[c]	ϵ_{3700}[c]
β-Nitrostyrene	16463	2922	687
Nitroform anion	2595	14847	7546
Nitroform	35	~ 0	~ 0

[a] ϵ for HA ~ 0 at 3100-3700 Å.
[b] Slit 0.64 mm.
[c] Slit 0.50 mm.

Ionization Constant of Nitroform.--The ionization constant of nitroform in methanol was determined by measurements of the concentration of the nitroform

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anion (from spectral data at 3500 Å) in solutions with known formal concentrations of anhydrous hydrogen chloride and nitroform.

Kinetic Studies with Pyridine Buffers.--In a typical run 0.002080 g. of HA was weighed into a 50-ml low-actinic glass volumetric flask and 45 ml of methanolic pyridine-pyridine hydrochloride buffer and 5 ml of 1.00 M methanolic sodium perchlorate, both at 25° were added. The solution was shaken and a sample placed in a quartz cell in the 25 ±0.1° thermostated cell compartment of the spectrophotometer. Optical density readings at 3700 Å were made at various times and for the points between 10 and 75% reaction first order rate constants were calculated from the equation

$$k = \frac{2.303}{t} \log \frac{D_\infty}{D_\infty - D}$$

where D is the optical density at time t and D_∞ that at infinite time. Test experiments showed that in the buffers used nitroform is present entirely as the anion, within experimental error. Our observed values of D_∞ as well as calculations based on the equilibrium constant show that the reaction proceeds essentially to completion under the conditions used.

The results obtained are listed in Table VI. In the experiments said to be at 38°, the absolute temperature is correct within 0.3° and the temperature held within 0.1° for any given run.

Kinetic Studies in Methanolic Hydrogen Chloride.--Reaction solutions were made up by adding standard methanolic hydrogen chloride to weighed samples of HA and then adding enough 1.00 M sodium perchlorate to bring the ionic strength to 0.100. At given times samples were pipetted from the reaction flask in a 40 ±0.1° bath into a spectrophotometer cell at 25° and the optical density

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TABLE VI

DECOMPOSITION OF HA IN A METHANOLIC PYRIDINE BUFFER AT 25°

([HA] = 1.385×10^{-4} M; $[C_5H_5N] = [C_5H_5NH^+] = 4.144 \times 10^{-3}$ M; $[NaClO_4] = 0.100$ M)

Time (sec.)	Optical Density[a]	$\log \frac{D_\infty}{D_\infty - D}$	$10^5 k$ (sec^{-1})
3960	0.151	0.0614	3.57
4560	0.173	0.0715	3.62
12360	0.411	0.1931	3.60
13560	0.441	0.2111	3.58
14760	0.468	0.2281	3.57
15960	0.496	0.2465	3.55
16560	0.510	0.2560	3.57
		Average	3.58 ±0.02

[a] $D_\infty = 1.150$, the calculated value is 1.140.

at 3100 and 3500 Å determined. From these measurements and the ionization constants of nitroform under these conditions, the concentrations of β-nitrostyrene and nitroform were calculated and substituted into the integrated form of the first order rate equation. The reaction was relatively slow and was only followed to about 20% of completion since β-nitrostyrene was found to decompose in methanol at a rate sufficient to have produced significant errors if we had tried to follow the reaction much further. Calculations based on K_E show that the reaction should proceed to more than 99% completion under the conditions used in these experiments.

Kinetics of the Addition of Nitroform to β-Nitrostyrene and Determination of K_E.--To 1.0518 g. of β-nitrostyrene in a 50-ml low-actinic volumetric flask were added 20 ml of 1.0380 M nitroform, 5 ml of 1.00 M sodium perchlorate and 25 ml of methanol. The flask was shaken, placed in a thermostated bath at

40 ±0.1°, and at measured times, 5-ml samples were transferred into 45 ml of ~0.5 M methanolic hydrogen chloride, to quench the reaction. A 5-ml aliquot of this was solution was then diluted to 100 ml with methanol to give a solution of which 5 ml was removed and diluted to 50 ml. Optical density measurements were made at 3100 and 3500 Å on this final solution which was 2000 times as dilute as the reaction mixture. From these measurements, the concentrations of reactants and products were calculated. The resultant data are listed in Table VII and plotted (open circles) in Fig. 2. Also plotted in Fig. 2 is a run made with $[HNF]_o = 0.0909$; $[NS] = 0.0713$; $[NaClO_4] = 0.000$.

TABLE VII

ADDITION OF NITROFORM TO β-NITROFORM IN METHANOL AT 40°

Time (hrs)	Optical Density 3100 Å	3500 Å	[NS][a]
0.0	0.583	0.135	0.1402
2.5	0.538	0.113	0.1340
4.5	0.503	0.119	0.1208
21.5	0.366	0.081	0.0884
24.5	0.356	0.076	0.0860

[a]Initial value of $[HNF]_{formal} = 0.4152$ M.

Runs used to determine the value of K_E were carried out similarly except that no sodium perchlorate was used, and in some cases HA was used as the reactant. The data obtained are plotted in Fig. 2.

Acknowledgments

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FINAL REPORT

PROJECT NO. A-282

THE ELECTRONIC PROPERTIES OF CERTAIN NITRO-CONTAINING SUBSTITUENT GROUPS

BY

JACK HINE AND WILLIAM C. BAILEY, JR.

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CONTRACT NO. NOrd-17063
DEPARTMENT OF THE NAVY

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NOVEMBER 6, 1957

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SUMMARY

The electronic properties of a number of substituent groups have been studied by a kinetic investigation of the reactions of a number of substituted acids with diphenyldiazomethane in ethanol. A relationship was found between the reaction rates of trans-3-substituted acrylic acids and the Hammett para sigma constant for the same substituents. From this relationship the sigma constant for the trinitromethyl, 1,1-dinitroethyl, 2-nitropropyl, and other groups was determined. From the data on both saturated and acrylic acids, Taft substituent constants were determined for a number of new nitro-containing groups. By both the Hammett and Taft constants the trinitromethyl group is shown to be the most strongly electron attracting uncharged substituent group known. The effect of acidity on the rates of reactions with diphenyldiazomethane is discussed briefly as is the reaction mechanism, which is believed to involve the formation of an ion pair as the rate-determining step.

INTRODUCTION

By the establishment of quantitative relationships in organic chemistry, earlier qualitative concepts have been modified and strengthened and new concepts have been developed. Probably the most useful of these relationships are the equations of Hammett[1,2] and Taft,[3,4] which express the electronic properties of various substituent groups and the sensitivity of various reactions to changes in electronic properties in numerical terms. While such electronic substituent constants have been determined for a large number of groups no determinations have been made for most of the groups of particular interest in aliphatic polynitro chemistry.

The purposes of this work were to obtain such data. Measurements on the rate of reaction of acids with diphenyldiazomethane have been used considerably for this purpose[5,6,7] and appeared to be particularly suitable for the present purpose, since the conditions required are mild enough to avoid degradation of the occasionally rather sensitive compounds to be studied. The previous workers had employed different sets of reaction conditions, of which those of

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(1) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Company, Inc., New York, N. Y., 1956, sec. 2-4e.

(2) H. H. Jaffé, Chem. Rev., 53, 191 (1953).

(3) Ref. (1), sec. 12-3 c.

(4) R. W. Taft, Jr. in M. S. Newman's, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1946, chap. 13.

(5) J. D. Roberts and C. M. Regan, J. Am. Chem. Soc., 74, 3695 (1952); 75, 4102 (1953); 76, 939 (1954); and earlier references cited therein.

(6) R. W. Taft, Jr., and D. J. Smith, ibid., 76, 305 (1954).

(7) A. B. Hoefelmeyer and C. K. Hancock, ibid., 77, 4746 (1955).

Roberts and Regan, 30° in an absolute ethanol solvent, seemed most convenient for us. The data of Taft and Smith, obtained at 25° in ethanol, should be easily corrected for the 5° temperature difference, especially since the activation energy of the reaction appears to be quite low. Comparison with the experiments of Hoefelmeyer and Hancock, carried out in toluene, would require a somewhat less reliable extrapolation.

RESULTS AND DISCUSSION

The rate constants obtained from the reaction of various acids with diphenyldiazomethane in absolute ethanol at 30° are listed in Table I. In each case the value shown is the mean of those obtained in several runs and in no case was the average deviation from the mean as much as 2.5 per cent. In the only direct comparison that can be made with published work our rate constant for benzoic acid is 4 per cent lower than that reported by Roberts, McElhill and Armstrong[8] which in turn is 4 per cent lower than the value of Roberts and Regan.[5] Errors of this order of magnitude would have no effect on any of the conclusions that have been reached in this investigation.

Hammett Substituent Constants.--Determination of Hammett sigma (substituent) constants by the ordinary methods was made impractical by the inaccessibility of the properly substituted aromatic acids. However, Dr. D. V. Sickman called our attention to the report by Charton that trans-3-substituted acrylic acids follow the Hammett equation.[9] According to Charton there is a good relationship between the dissociation constants of these acids and Hammett's para sigma constants. A similar relationship is said to exist for trans-3-substituted maleic and 3-methylacrylic acids. Aside from a few cinnamic acid derivations, however, it is not clear just what compounds were studied. In Fig. 1 is a plot of log k for six of our 3-substituted acrylic acids[10] versus the appropriate para sigma constants (values taken from the collection by Jaffe[12]).

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(8) J. D. Roberts, E. A. McElhill and R. Armstrong, ibid., 71, 2923 (1949).

(9) M. Charton, Abstracts of Papers Presented at the 130th National Meeting of the American Chemical Society, Atlantic City, New Jersey, September 16-21, 1956, p. 83-O.

(10) For a discussion of whether these compounds were actually trans or not see the Experimental section.

TABLE I

RATE CONSTANTS FOR REACTION OF ACIDS
WITH DIPHENYLDIAZOMETHANE IN ETHANOL AT 30°

Acid[a]	k(l. mole^{-1} min^{-1})	log k
$CH_3CH{=}CHCO_2H$	0.61	-0.215
$CH_2{=}CHCO_2H$	1.27	0.104
$ClCH{=}CHCO_2H$	2.48	0.394
$CH_3COCH{=}CHCO_2H$	4.03	0.605
$HO_2CCH{=}CHCO_2H$	6.71	0.826
$Cl_2CHCH{=}CHCO_2H$	2.36	0.373
$Cl_3CCH{=}CHCO_2H$	5.39	0.732
$O_2NCH{=}CHCO_2H$	21.8	1.338
cis-$O_2NC(CH_3)_2CH{=}CHCO_2H$	3.47	0.540
trans-$O_2NC(CH_3)_2CH{=}CHCO_2H$	2.49	0.396
$CH_3C(NO_2)_2CH{=}CHCO_2H$	11.5	1.061
$C_2H_5C(NO_2)_2CH{=}CHCO_2H$	13.0	1.114
$(O_2N)_3CCH{=}CHCO_2H$	25.3	1.403
$C_2H_5C(NO_2)_2CH_2CH_2CO_2H$	2.18	0.338
$CH_3C(NO_2)_2CH_2CH_2CO_2H$	2.03	0.308
$(O_2N)_3CCH_2CH_2CO_2H$	3.76	0.575
$C_6H_5CO_2H$	1.00	0.000
saccharin	19.1	1.282

[a]Except for the β-acetylacrylic acid and one labelled "cis", all of the substituted acrylic acids are believed or known to be trans. For the relevant evidence see the Experimental section.

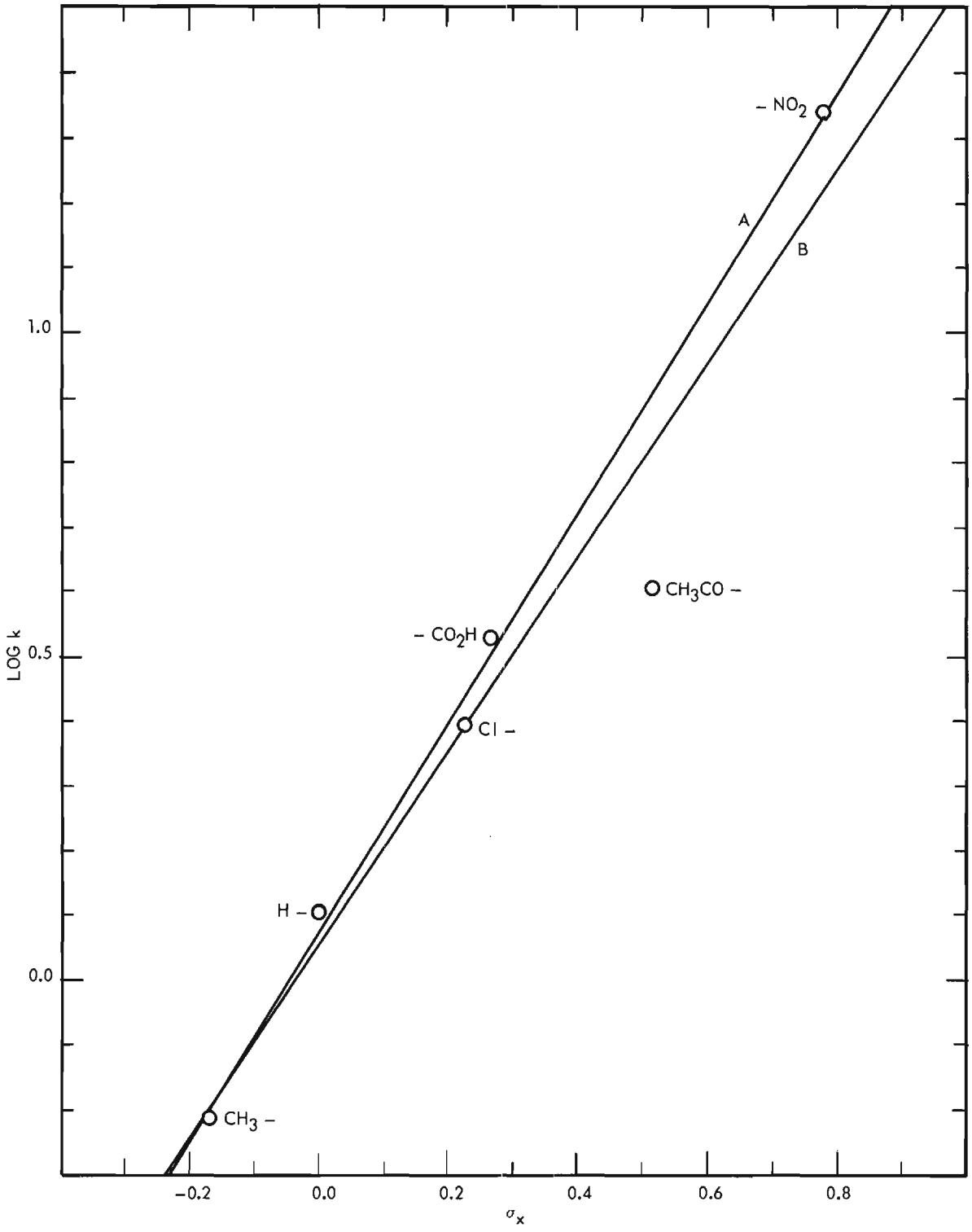

Figure 1. Log k for Trans-3-X-Acrylic Acids Versus σ_x.

The point for the acetyl compounds deviates considerably from line A, which was determined to be the best line through the other points by the method of least squares. In the Hammett equation

$$\log k = \log k_o + \rho\sigma \qquad (1)$$

the values 0.072 for log k and 1.623 for ρ give line A. From the equation and these two values σ constants were calculated for the other groups studied, using the relation

$$\sigma = \frac{\log k - 0.072}{1.623}$$

Line B was calculated by the least squares method using all of the data (including that for the acetyl compound), and corresponds to a log k_o value of 0.056 and a ρ value of 1.495. The new σ values calculated from lines A and B are listed in Table II. The deviation of the acetyl compound might appear to be in the wrong direction to be explained by the suggestion that the acid employed is cis, since the usually greater acidity of cis acids and our observation of the greater reactivity of the cis isomer of 4-nitro-4-methylpentenoic acid would lead one to expect the cis-β-acetylacrylic acid to be faster rather than slower than predicted from line A of Fig. 1. However, as described in the experimental section (under Stereochemistry of the Acrylic Acids), Shaw has found evidence that the compound exists largely in the pseudoacid form.[11] For this reason we believe that the data obtained by use of line A is more reliable.

(11) E. Shaw, J. Am. Chem. Soc., 68, 2510 (1946).

TABLE II

HAMMETT SUBSTITUENT CONSTANTS FROM FIG. 1

Substituent Group	σ from A[a]	σ from B[b]
$(O_2N)_3C$-	0.820	0.901
$CH_3C(NO_2)_2$-	.609	.672
$O_2NC(CH_3)_2$-	.200	.227
$C_2H_5C(NO_2)_2$-	.642	.708
Cl_3C-	.407	.452
Cl_2CH-	.185	.212

[a] Ignoring the point for the acetyl compound.
[b] Including the point for acetyl.

While the new σ constants listed in Table II do not serve to show how much of the effects of the various groups is inductive and how much is resonance, they do establish the trinitromethyl groups as the most strongly electron-withdrawing electrically neutral group for which a σ constant has been determined. The σ values obtained can be seen to be plausible in several respects. Thus while the trichloromethyl group is electron-withdrawing it is not as strongly electron-withdrawing as the trifluoromethyl group for which a para σ constant of +0.551 has been found. Furthermore, Fig. 2 shows that with one exception the electron-withdrawing power of a given type of substituent increases steadily as more and more chlorine atoms or nitro groups are included in it. The sole exception is not a large one and would be eliminated by an error of 0.1 in the σ value for chloromethyl group reported by Jaffé or in the value we obtained for the

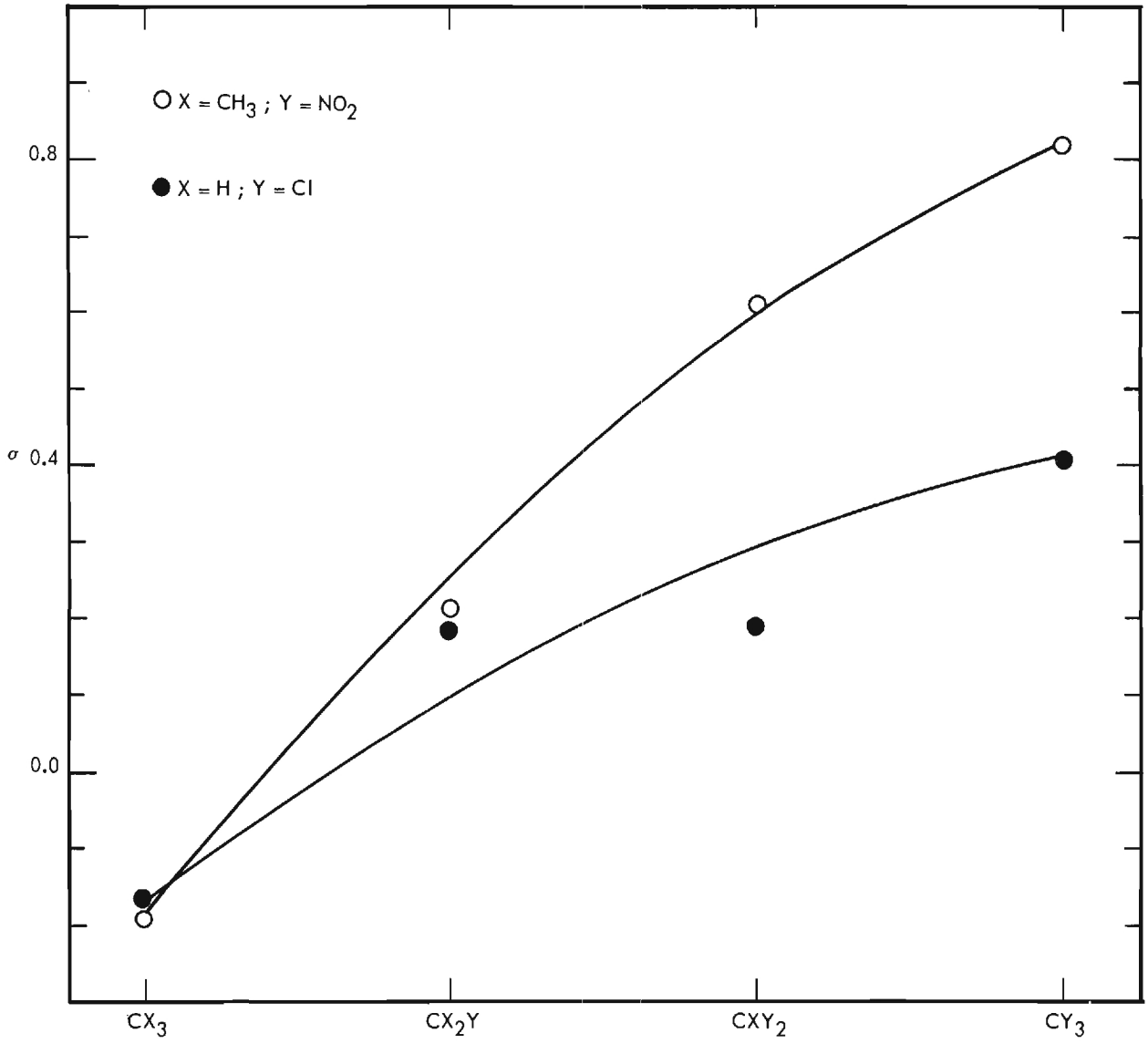

Figure 2. Changes in σ with Systematic Changes in Structure of Substituent.

dichloromethyl group. The curvature in the best lines through each of the two sets of points suggests a saturation effect. That is, the introduction of successive electron-withdrawing groups has a diminishing effect on the reactivity.

Taft Substituent Constants.--For the purpose of determining Taft substituent constants our data was combined with that of Taft and Smith.[6] We find benzoic acid to react 1.05 times as fast and Roberts and Regan found it to react 1.13 times as fast at 30° as Taft and Smith did at 25° and Roberts and Regan found acetic acid to react 1.21 times as fast at 30° as Taft and Smith did at 25°. After averaging these data we corrected Taft and Smith's data to 30° by adding 0.051 to log k for each value. While this procedure is not completely rigorous the entire correction is so small that any deviations from it should be very small. The resultant data are listed in Table III and plotted against Taft's

TABLE III

TAFT AND SMITH'S VALUES OF LOG k CORRECTED TO 30°

Acid	log k	Acid	log k
$CNCH_2CO_2H$	1.318	$C_6H_5CH_2CO_2H$	0.218
$ClCH_2CO_2H$	1.162	$C_6H_5CH_2CH_2CO_2H$	.088
$C_6H_5CH(OH)CO_2H$	0.882	$C_6H_5CO_2H$	.033
$HOCH_2$	.530	CH_3CO_2H	- .283
$(C_6H_5)_2CHCO_2H$	.418	$n\text{-}C_5H_{11}CO_2H$[a]	- .304
HCO_2H	.399	$t\text{-}BuCO_2H$	- .478
$ClCH_2CH_2CO_2H$	.401	$C_6H_5C{\equiv}CCO_2H$[b]	1.292

[a] Since Taft does not appear to have listed a substituent constant for the n-amyl group we have used the value (0.162) reported by Hoefelmeyer and Hancock.[7]

[b] This value is from the work of Roberts and Carboni.[12]

substituent constants in Fig. 3. Also plotted are the data on the only two other compounds for which the rate data and the relevant Taft polar substituent constants are available. These are crotonic acid, which we studied, and phenylpropiolic acid which was studied by Roberts and Carboni.[12] As Taft and Smith have pointed out, benzoic acid reacts much more slowly than would be expected from the polar substituent constant. The point for crotonic acid deviates in the same direction and by almost as large an amount as that for benzoic acid. The point for phenylpropiolic acid also deviates in the same direction, but by a much smaller, though probably significant, amount. As Taft and Smith suggest for the case of benzoic acid this is probably due to the resonance of carboxyl carbonyl group with the group attached thereto. Taft had previously estimated that there is about 700 cal/mole less of such resonance in the benzoate anion than in benzoic acid.[13] From Fig. 3 it may be estimated that 760 cal of such resonance has been lost in the transition state for reaction with diphenyldiazomethane by benzoic acid, 700 cal. for crotonic acid, and 240 cal for phenylpropiolic acid. The latter factor suggests that α,β triple bonds enter into much less resonance with carbonyl groups than do α,β double bonds and directly attached aromatic rings. From the first two factors it appears, as Kreevoy and Taft have shown more convincingly[14], that aromatic rings and α,β-unsaturated double bonds resonate about equally well with carbonyl groups. For this reason we have assumed that the points for all trans-3-substituted acids should fall on a line parallel

(12) J. D. Roberts and R. A. Carboni, J. Am. Chem. Soc., 77, 5554 (1955).

(13) R. W. Taft, Jr., ibid., 75, 4237 (1953).

(14) M. M. Kreevoy and R. W. Taft, Jr., ibid., 79, 4016 (1957).

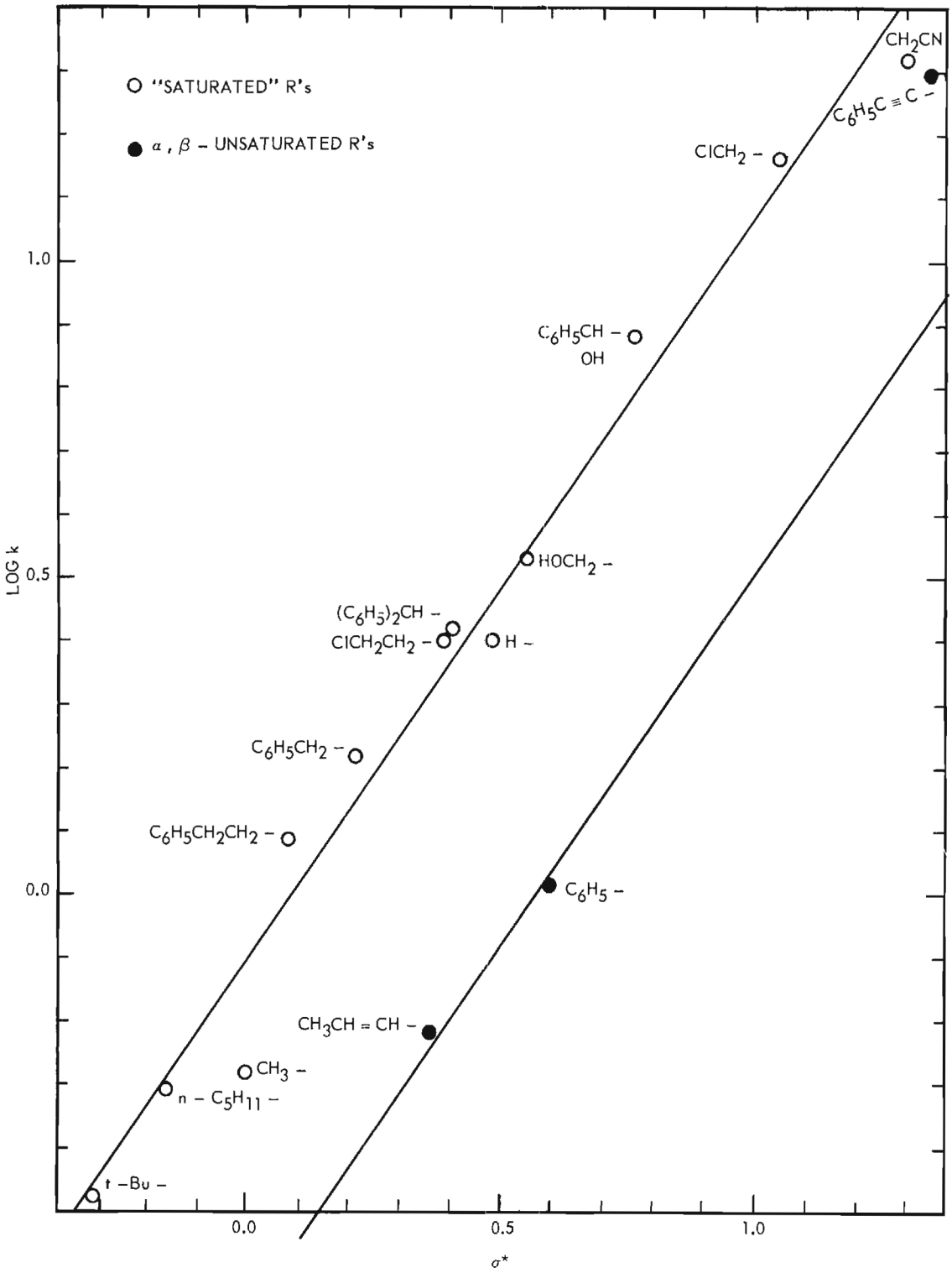

Figure 3. Log k for Reaction of RCO_2H with Diphenyldiazomethane Versus σ^* (Taft and Smith).

to that for the unsaturated acids and including as well as possible the points for crotonic and benzoic acids.

The Taft equation,

$$\log k = \log k_o + \rho^* \sigma^* \qquad (2)$$

for the upper line has the form

$$\log k = -0.105 + 1.174\ \sigma^* \qquad (3)$$

when the optimum values of $\log k_o$ and ρ^* were calculated by the method of least squares. For the lower line the equation is

$$\log k = -0.663 + 1.174\ \sigma^* \qquad (4)$$

The values of σ^*, the Taft substituent constant, calculated from eq. 3 for saturated groups and from eq. 4 for α,β-unsaturated groups are listed in the left hand column of Table IV. By comparison of the σ^* constant of the $(O_2N)_3CCH_2CH_2$-group with those of the $O_2NCH_2CH_2$-, $ClCH_2CH_2$- and $CF_3CH_2CH_2$- groups, the most strongly electron-withdrawing mono-β-substituted ethyl groups upon which data is available, it appears that the trinitromethyl group is the most strongly electron-withdrawing group known. From the directly determined values of σ^* for various XCH_2- groups the σ^* value for the X-groups have been estimated by multiplication by 2.8.[15]

The Taft polar substituent constant for a group attached to the reaction center through a saturated chain depends only on the inductive effect of the

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(15) cf. ref. (4), sec. V-2b and Table XIb.

TABLE IV

TAFT POLAR SUBSTITUENT CONSTANTS

R	σ^* [a]	R	σ^*
$(O_2N)_3CCH_2CH_2$-	+0.579	$O_2NCH_2CH_2$-	+0.50 [b]
$C_2H_5C(NO_2)_2CH_2CH_2$-	.377	$ClCH_2CH_2$-	.385 [b]
$CH_3C(NO_2)_2CH_2CH_2$-	.352	$CF_3CH_2CH_2$-	.32 [b]
$(O_2N)_3CCH$=CH-	1.759	$(O_2N)_3CCH_2$-	1.62 [c]
O_2NCH=CH-	1.704	$C_2H_5C(NO_2)_2CH_2$-	1.06 [c]
$C_2H_5C(NO_2)_2CH$=CH-	1.513	$CH_3C(NO_2)_2CH_2$-	.99 [c]
$CH_3C(NO_2)$CH=CH-	1.468	$(O_2N)_3C$-	4.54 [c]
Cl_3CCH=CH-	1.188	$C_2H_5C(NO_2)_2$-	2.96 [c]
CH_3COCH=CH-	1.080 [d]	$CH_3C(NO_2)_2$-	2.76 [c]
HO_2CCH=CH-	1.012	O_2NCH_2-	1.40 [c]
$O_2NC(CH_3)_2CH$=CH-	0.910	O_2N	3.94 [c]
ClCH=CH-	.900	CF_3CH_2-	0.92 [b]
Cl_2CHCH=CH-	.882	CF_3-	2.58 [c]
CH_2=CH-	.653		

[a] All values in this column calculated from eqs. 3 and 4.

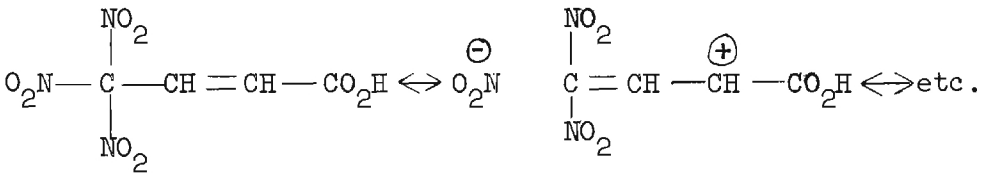
[b] From ref (4), p. 619.

[c] Values of σ^* for X- obtained by multiplying the value for XCH_2- by 2.8.

[d] This value is probably unreliable because the acetylacrylic acid appears to have been in the pseudoacid form.

group, while the Hammett σ constant measures both the inductive and resonance effects. Since the Taft σ^* constant for the trinitromethyl group is 16 per cent

larger than that for the nitro group, the Hammett σ constant should be considerably less than 16 per cent larger if the effect of the trinitromethyl group is solely inductive, since the σ constant of the nitro group is known to contain a considerable contribution from resonance. Table II shows that Hammett's σ is 5-16% larger for the trinitromethyl than for the nitro group. It therefore seems probable that the trinitromethyl group has some resonance effect. This resonance effect appears to be smaller than that of the nitro group, but because of the uncertainties in the σ's and σ^*'s we cannot be very sure of this latter conclusion. The resonance effect of the trinitromethyl group is probably due to the contribution of certain no bonded structures analogous to those suggested for the trifluoromethyl group by Roberts, Webb and McElhill.[16]



Correlation of Reaction Rates with Acidity.--It is clear that the reactivities of carboxylic acids should be reasonably well correlated with their ionization constants since both the rates and the ionization constants may be correlated well with the Taft substituent constants. It is of interest, however, to see how the reactivities of noncarboxylic acids fit into such a relationship. For this purpose values of log k have been plotted against values of pK in ethanol in Fig. 4. Much of the available rate data could not be plotted due to the inaccessability of pK values in ethanol. The pK values for acetic, formic,

(16) J. D. Roberts, R. L. Webb and E. A. McElhill, J. Am. Chem. Soc., 72, 408 (1950).

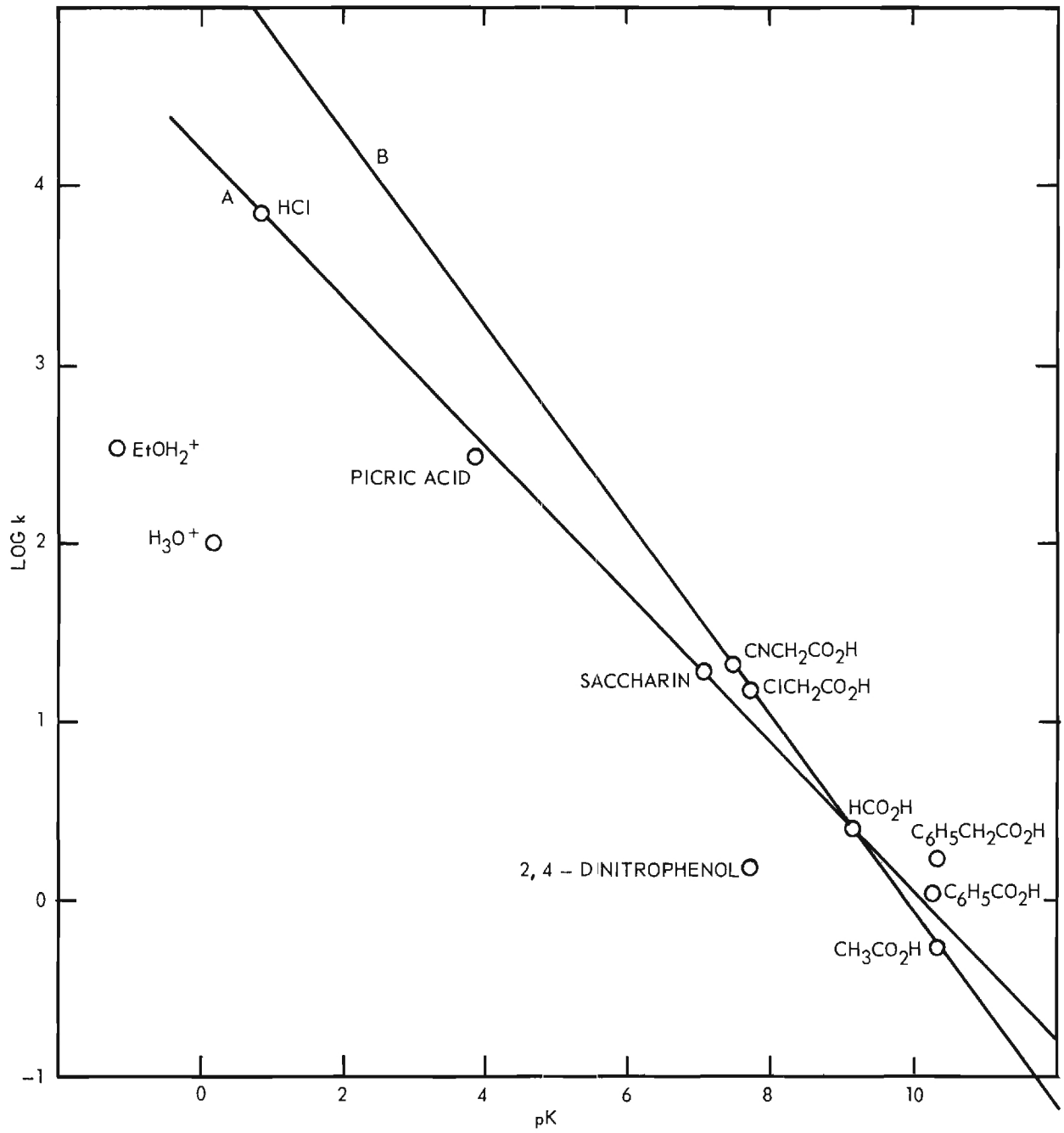


Figure 4. Plot of Log k for Reaction of HA with Diphenyldiazomethane Versus the pK of HA.

benzoic and cyanoacetic acids are those listed by Grunwald and Berkowitz,[17] and those for chloroacetic acid, 2,4-dinitrophenol and picric are from the work of Deyrup.[18] The values for the hydronium ion and hydrogen chloride are from Bezman and Verhoek.[19] The value for the ethyloxonium ion follows from a definition of terms as -log 17 since pure ethanol is about 17 molar. The k values for ethyloxonium ion is from the work of Roberts and Watanabe,[20] the value for the hydronium ion was estimated as about 100 from their Figs. 3 and 4, and a value of 7000 for hydrogen chloride estimated from their footnote 34 and Fig. 6.

It is clear from our Fig. 4 that the oxonium (hydronium) ion and its ethyl derivative are much less reactive than would be expected from their acidities. This may be in some way related to the fact that these two acids are of a different electrical charge type from the others. The reactivity of 2,4-dinitrophenol is also low although by a smaller amount, and the related compound, picric acid, while in reasonable agreement with line A, deviates almost as much as the dinitrophenol from B, a line through the best points for aliphatic carboxylic acids. Perhaps this deviation results from the internal hydrogen bonding between the phenolic hydrogen atom and the hydroxyl group ortho to it.

Mechanism of the Reaction of Diphenyldiazomethane with Acids.--The mechanism of the reaction of diphenyldiazomethane with acids in ethanol has been studied most thoroughly by Roberts and co-workers. Staudinger, Anthes and Pfenninger had

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(17) E. Grunwald and B. J. Berkowitz, J. Am. Chem. Soc., 13, 4939 (1951).

(18) A. J. Deyrup, ibid., 56, 60 (1934).

(19) I. I. Bezman and F. N. Verhoek, ibid., 67, 1330 (1945).

(20) J. D. Roberts and W. Watanabe, ibid., 72, 4869 (1950).

previously found that in the absence of added acids diphenylketazine, $(C_6H_5)_2C=N-N=C(C_6H_5)_2$, is the major reaction product and benzhydryl ethyl ether is a by-product of a rather slow thermal decomposition that is strongly catalyzed by light.[21] Roberts and Watanabe found that in the presence of p-toluenesulfonic acid, benzhydryl ethyl ether is formed in greater than 95-% yield,[20] in a reaction that is first order in acid and first order in diazo compound. They also state that the reaction is subject to a deuterium kinetic isotope effect of about five-fold, and is general-acid catalyzed, with undissociated hydrogen chloride apparently being a very effective catalyst. The reaction with benzoic acid in ethanol was studied by Roberts, Watanabe and McMahon who observed that although the reaction was clearly first order in benzoic acid, only 60 per cent of the reaction product was benzhydryl benzoate (the rest being benzhydryl ethyl ether) and the addition of large amounts of benzoate ion did not increase the yield of benzhydryl benzoate significantly.[22] Because of this latter observation it was stated that the organic benzoate could not have been formed by the reaction of benzhydryl carbonium (or diazonium) ions with benzoate ions or ethanol competitively because in such a case the increase in benzoate ion concentration should have been accompanied by an increase in the fraction of benzhydryl benzoate produced. Instead, the most plausible mechanism was felt to be a concerted process in which nitrogen was expelled from the diphenyldiazomethane molecule by the simultaneous attack of the acidic hydrogen and one of the two oxygen atoms of the benzoic acid. The benzhydryl ethyl ether produced simultaneously cannot

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(21) H. Staudinger, E. Anthes, and F. Pfenninger, Ber., 49, 1928 (1916).

(22) J. D. Roberts, W. Watanabe and R. E. McMahon, J. Am. Chem. Soc., 73, 760 (1951).

be formed by a concerted process since it is partially replaced as a product by benzhydryl thiocyanate when thiocyanate ions are added to the solution although the thiocyanate ions have no effect on the reaction rate. These authors also studied the reaction with 2,4-dinitrophenol[23] for which an analogous mechanism was suggested, and the possibility of another mechanism involving the rate controlling formation of an ion-pair mentioned. This latter mechanism

$$(C_6H_5)_2CN_2 + HX \rightarrow C_6H_5CHN_2^+ + X^-$$

$$(C_6H_5)_2CHN_2^+ \; X^- \rightarrow (C_6H_5)_2CHX + N_2$$

seems the most plausible to us. The correlation of reaction rate with acidity of the catalyzing acid is most simply explained by the rate controlling step being a simple proton donation. So also is the deviation of the points for benzoic and crotonic acids from the line through the rest of the points in Fig. 3. As previously implied, the magnitude of this deviation is in excellent agreement with that which would be expected if the catalyst portion of the transition state had a large amount of carboxylate ion character. There are several arguments that may be used to establish the fate of this initially formed benzhydryl diazonium carboxylate ion pair. Although the S_N1 reactivity of benzhydryl compounds is quite high, their S_N2 reactivity is probably not nearly as well developed. We therefore assume that both the ester and ether are formed through the intermediacy of the benzhydryl carbonium ion. In this connection it is worthwhile to point out that since Roberts and Watanabe state that the by-product

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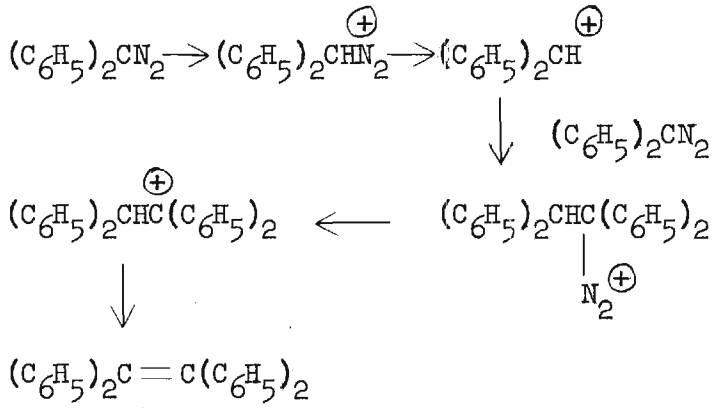
(23) idem., ibid., 2521 (1951).

tetraphenylethylene is formed only in the acid catalyzed reaction, its formation may occur by the following mechanism.



If this hypothesis is correct the yield of tetraphenylethylene should increase with increasing diphenyldiazomethane concentration. If, then, both ester and ether are formed from the carbonium ion, the principal remaining problem is whether the ether is formed from carbonium ions derived from diazonium ions that dissociated from carboxylate ions before losing nitrogen, or whether it is formed from carbonium ions that were formed in an ion-pair that subsequently dissociated, or both. If the deviation of ester yield from 100 per cent is largely due to dissociation of the diazonium-carboxylate ion pair before it has a chance to lose nitrogen, then this deviation should be larger with a related compound that would form a less stable carbonium ion, and hence whose diazonium ion would lose nitrogen more slowly. On the other hand, if the deviation were due to the diffusion of the carbonium ion-carboxylate ion-pair apart before they combined, it should be smaller with a compound that should form less stable and hence more reactive carbonium ions. The latter alternative seems more probable for two reasons. First, data on the diazotization of aliphatic amines suggests

that even saturated primary aliphatic diazonium cations have a very strong tendency to lose nitrogen to give carbonium ions. With the benzhydryl diazonium cation this process should be so tremendously faster that even the dissociation of an ion-pair would find it difficult to keep pace with it. Second, the rate of collapse of a carbonium ion-carboxylate ion pair to an ester should be much more sensitive to the structure of the carboxylate ion than should the rate of dissociation of diazonium ion-carboxylate ion pair. Therefore the increase in ester yield from about 60 per cent with benzoic acid to 87 per cent with acetic acid[5] suggests that the smaller and more nucleophilic acetate ion is better able to combine with the benzhydryl carbonium ion before it escapes by diffusion.

EXPERIMENTAL

All melting points and boiling points are uncorrected. All chemicals used were of reagent grade or were purified from procedures described in the literature. Special care was taken to ensure the anhydrous character of the absolute ethanol used in the kinetic runs. Commercial absolute ethanol was dried repeatedly by treatment of the alcohol with an excess of diethyl phthalate and sodium ethoxide, formed in situ. After several hours reflux, the alcohol was distilled directly through a 1.5-meter vacuum-jacketed column into a dried receiver. The alcohol was stored in 500-ml. volumetric flasks, the necks of which were sealed with a small film of silicon grease applied to the ground glass surfaces. Each flask of alcohol was used for no more than three kinetic runs. The remainder of the alcohol was saved for "redrying."

The nitro acids in this report were kindly furnished by the Organic Chemistry Division, U. S. Naval Ordnance Laboratory, Silver Spring, Maryland. These compounds were stored unopened in a refrigerator and dried before use over either potassium hydroxide or phosphorous pentoxide in a desiccator under a slight vacuum. The remainder of the compounds studied were purified reagent grade material or prepared in this laboratory. These preparations were made from procedures or adaptations of procedures described in the literature.

Benzophenone Hydrazone.--Benzophenone hydrazone was readily prepared from benzophenone and 95% hydrazine hydrate.[24]

Diphenyldiazomethane.--Diphenyldiazomethane was prepared when needed as described by Smith and Howard.[24] The crude diphenyldiazomethane was dried over potassium

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(24) L. I. Smith and K. L. Howard, Organic Synthesis, Collective Vol. III, p. 351.

hydroxide for 4 hours at 1-2 mm. pressure and diluted to a usable concentration with anhydrous ethanol. This solution was stored in acitinic glassware at 5-10°C.

α,β-Dibromopropionic Acid[25].-- Reaction of methyl acrylate with bromine gave a 93% yield of methyl α,β-dibromopropionate. Treatment of this bromo-ester with 20% aqueous hydrobromic acid at the boiling point for 5 hours furnished in 56% yield, α,β-dibromopropionic acid, 134-135°/24 mm.

Ethyl Vinylglycolate[26].--Acrolein cyanohydrin was prepared by reaction of acrolein and glacial acetic acid in an ether solution with sodium cyanide. Treatment of acrolein cyanohydrin with an ethanolic solution saturated with dry hydrogen chloride afforded crystalline hydroxy-imidoether hydrochloride, which was hydrolyzed in situ by the addition of the calculated amount of water and heating the mixture under reflux for 15 minutes. An overall 35% yield of the desired ethyl vinylglycolate, b.p. 68°/15 mm. was obtained. The reported boiling point is 66°/13 mm.

Treatment of Ethyl Vinylglycolate with Phosphorus Trichloride.--A procedure for the reaction of ethyl vinylglycolate with phosphorus tribromide to obtain ethyl γ-bromocrotonate is reported.[26] Further, it is reported that ethyl γ-chlorocrotonate is readily hydrolyzed to the free acid using barium hydroxide.[27]

Treatment of ethyl vinylglycolate with phosphorous trichloride using Braun's procedure gave 28% unchanged ethyl vinylglycolate. The remainder of the

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(25) C. S. Marvel, J. Am. Chem. Soc., 62, 3495 (1940).

(26) J. W. E. Glattfield and R. E. Hoen, J. Am. Chem. Soc., 57, 1405 (1935); J. W. E. Glattfield and E. C. Lee, ibid., 62, 354 (1940).

(27) G. Braun, J. Am. Chem. Soc., 52, 3167 (1930).

material could not be distilled without extensive decomposition even at 1 mm. The dark, semi-solid material resinifies below 75°.

Treatment of ethyl vinylglycolate with thionyl chloride in pyridine-ether solution at 25° gave 92% unchanged starting material after 3 days. The remainder of the reacting material was converted to a polymeric substance.

Treatment of ethyl vinylglycolate with dry hydrogen chloride in ether solution at 0° for one hour afforded a residue having a positive Beilstein test for halogen. This material was hydrolyzed with barium hydroxide yielding a small amount of a glass material that was recrystallized from hexane. This material had a melting range of 91-92°. The melting point reported for trans-γ-chlorocrotonic acid is 83°. The reported melting point of β-chloroisocrotonic acid corresponds to that obtained here.

Preparation of β-Acetylacrylic Acid[28].--β-Acetylacrylic acid was readily prepared by treatment of levulinic acid with bromine in hydrochloric acid solution to afford the crude β-bromolevulinic acid. Treatment of this material with freshly fused sodium acetate in glacial acetic acid afforded the desired β-acetylacrylic acid.

Preparation of γ,γ,γ-Trichlorocrotonic Acid[29].--The preparation of γ,γ,γ-trichlorocrotonic acid was effected by the addition of chloral hydrate to malonic acid in pyridine. The mixture was heated at 80-85° for 4 hours, cooled and water added. Treatment of the purified γ,γ,γ-trichloro-β-hydroxy-butyric acid obtained with sodium acetate in acetic anhydride at 80-85° for 3 hours gave

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(28) W. G. Overend, L. M. Turton and L. F. Wiggins, J. Chem. Soc., 3500 (1950).

(29) K. v. Auwers, Ber., 56B, 715, 731 (1923).

γ,γ,γ-trichlorocrotonic acid, m.p. 112-112.5°. The reported melting point is 113.5-114°. This material was recrystallized from hexane to obtain material of the reported melting point.

Preparation of trans-β-Chloroacrylic Acid[30].--Propiolic acid was prepared according to Ingold[31] from the mono-potassium salt of acetylenedicarboxylic acid. The yield was 65 per cent of pure product, b.p. 75-76°/22 mm.

Propiolic acid, 45.5 g. (0.65 mole) was added to 65 g. of concentrated hydrochloric acid. The solution was heated at 60° for one hour and then cooled to 10°. The trans acid separated from solution as thin plates and was removed by suction filtration. The trans acid was redissolved in 100 ml. of hot water and the solution treated with 1.0 g. of Norite. After removal of the Norite by filtration, 50 ml. of concentrated hydrochloric acid was added to the solution and the mixture reheated to dissolve precipitated product. The product obtained upon cooling the solution was again recrystallized from dilute hydrochloric acid as above to obtain 12.7 g. of pure trans-β-chloroacrylic acid, m.p. 84°.

Preparation of γ,γ-Dichlorocrotonic Acid[32].--Twenty grams of pure γ,γ,γ-trichlorocrotonic acid (0.105 mole) was dissolved in 40 ml. of absolute ethanol and 15.5 ml. of glacial acetic acid was then added. To this solution, 9.0 g. of zinc dust (0.137 mole) was added over 25 minutes. The temperature of the solution was maintained at 55-60° during the zinc dust addition and the solution was stirred vigorously throughout. The solution was stirred an additional 15 minutes,

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(30) H. J. Backer and A. E. Beute, Rec. trav. chim., 54, 167 (1935).

(31) C. K. Ingold, J. Chem. Soc., 127, 1199 (1925).

(32) J. W. E. Glattfield and E. Reitz, J. Am. Chem. Soc., 62, 976 (1940).

cooled, and 200 ml. of water was added. The solution was extracted with three 50-ml. portions of ether; the ether extracts were combined and washed with three 15-ml. portions of water. The ether was removed under diminished pressure and the residue distilled to obtain 13.2 g. of crystalline material, b.p. 90°/1 mm. (Reported b.p. 110°/2 mm.). The crystalline material was dissolved in the minimum amount of boiling hexane, cooled to 5°C and collected by suction filtration. The purified product weighed 10.7 g. and had m.p. 42°. The reported melting point is 42-43°.

Attempted Preparation of trans-β-Methoxyacrylic Acid[33].--α,β-Dibromopropionic acid (100 g., 0.434 mole) was dissolved in 80 ml. of warm anhydrous methanol. This solution was added to a warm solution (35°) of methanolic sodium methoxide prepared by the addition of 38 g. of sodium (1.65 g. atom) portionwise to 600 ml. of anhydrous methanol. After the vigorous reaction had subsided, the mixture was heated under reflux for 7 hours. The methanol was then removed under diminished pressure. The dried residue was dissolved in 300 ml. of water and the resulting solution cooled in an ice bath. With cooling, 250 ml. of 5% aqueous hydrochloric acid was added. The acidified mixture was rapidly extracted with five 150-ml. portions of ether. The combined ether extracts were washed with two 25-ml. portions of water. The ether was then removed at the water pump to obtain 6.2 g. of a slightly yellow oil. The oil was fractionated through a standard Todd column; obtained 5.8 g. of clear oil, b.p. 108°/5 mm. Attempts to obtain this material crystalline were fruitless. The material is soluble in water, whereas it is reported[33] that trans-β-methoxyacrylic acid recrystallizes

(33) L. N. Owen and H. M. B. Somade, J. Chem. Soc., 1030 (1947).

from water and has a melting point of 102°. The material could not be obtained crystalline from ligroin, benzene or by partial freezing in a solid carbon dioxide-chloroform cooling bath.

Other attempts to prepare this compound using the same procedure gave a small yield of oil which could not be induced to crystallize and, also, was soluble in water.

Preparation of p-Hydrazinobenzoic Acid[34].--p-Hydrazinobenzoic acid was prepared in high yield using the method of Veibel. p-Aminobenzoic acid was treated in the cold with sodium nitrite in acid solution. The diazonium compound formed was treated directly with aqueous sodium sulfite. Isolation of the hydrazino-acid was readily effected upon addition of concentrated hydrochloric acid. Crystalline material, m.p. 238-243°, was isolated in 89% yield. The melting point of pure p-hydrazinobenzoic acid is reported as 240-250°, dependent upon the rate of heating of the crystalline material.

Attempted Preparation of p-Azidobenzoic Acid[35].--p-Hydrazinobenzoic acid, 15.2 g. (0.10 mole) was dissolved in a solution prepared from 100 ml. of water and 20 ml. of concentrated hydrochloric acid. The mixture was warmed slightly to effect solution. The solution was cooled to 0°C and 50 ml. of ether was added. The mixture was rapidly stirred while a previously prepared solution of 10 g. of sodium nitrite in 10 ml. of water was added at such a rate that the temperature remained below 5°C.

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(34) S. Veibel, Bull. Soc. Chim. France, (5) 5, 1507 (1938).

(35) Cf., Organic Syntheses, Vol. 22, p. 96.

The evolution of a considerable amount of gas was noted and the mixture assumed a dark orange color. After stirring for 15 minutes further, a 50-ml. portion of ether was added. The ether layer was separated and the water layer extracted with two 25-ml. portions of ether. The ether extracts were combined with the initial ether solution and this then washed with three 15-ml. portions of water. After drying the solution over 10 g. of anhydrous sodium sulfate the ether was removed under reduced pressure. A dark plastic glass weighing 16.8 g. was obtained. This material was practically insoluble in the common organic solvents and decomposed on standing. Attempts to purify the material from ethanol-water, benzene and ligroin were not successful.

Reaction of p-Aminobenzoic Acid with Chloroform and Base[36].--Thirty grams of pure p-aminobenzoic acid (0.219 mole) was dissolved in 43 ml. of reagent grade chloroform (0.535 mole) with heat. This solution was added in small portions to a well-stirred solution of 61 g. of potassium hydroxide (1.09 mole) in 160 ml. of absolute ethanol maintained at 55-60°. The mixture was heated at 55-60° for 10 minutes upon completion of the addition. The mixture was evaporated to dryness at the water pump and 400 ml. of water was added. The solution was acidified to a pH of 4 with 5-% aqueous hydrochloric acid and extracted with three 75-ml. portions of ether. The combined ether extracts were washed with 100 ml. of water, three 100-ml. portions of 5-% aqueous hydrochloric acid and finally with three 100-ml. portions of water. The ether solution was dried over 25 g. of anhydrous sodium sulfate for 15 minutes, the drying agent removed by filtration and the ether removed at the water pump. A dark, viscous oil,

(36) Cf. C. K. Ingold, J. Chem. Soc., 125, 87 (1924); N. V. Sidgwick, ibid., 1876 (1930).

8.7 g., was obtained. Attempts to purify this material were not investigated further after it was noted that extensive decomposition (gas evolution) was taking place in both benzene and aqueous ethanolic solutions of the crude material when warmed no higher than 70°.

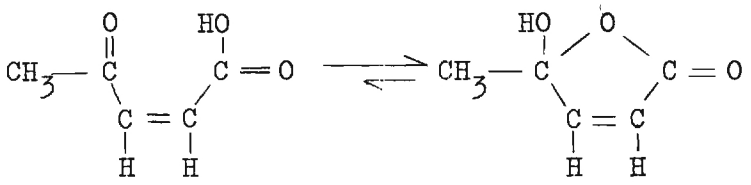
Reaction of p-Bromobenzoic Acid with Silver Cyanide.--Two further attempts to prepare p-isocyanobenzoic acid were tried. p-Bromobenzoic acid was treated with silver cyanide in ether solution for 3-1/2 days. A recovery of 94-percent unchanged p-bromobenzoic acid was effected. The experiment was repeated with benzene used as solvent. The mixture was heated under reflux for 6 hours. Filtration of the mixture and evaporation of the solvents gave 8.7 g. of a heavy oil which was soluble in all common organic solvents except petroleum ether. By slurring the oil with petroleum ether, a 31-% recovery of starting p-bromobenzoic acid was effected. The remainder of the crude product decomposed as noted above and was discarded.

Attempted Allylic Chlorinations of Crotonic Acid and Methyl Crotonate.--Five grams of crotonic acid was dissolved in 25 ml. of glacial acetic acid and the solution heated to 60°. N-Chlorosuccinimide, 8:55 g., was added in small portions over 10 minutes. The solution was then heated at 80° for 4 hours. Upon cooling the solution, 8.4 g. of N-chlorosuccinimide, m.p. 144-147°, was recovered.

Allylic chlorination of methyl crotonate was also attempted. Ten grams of methylcrotonate (0.10 mole) was dissolved in 50-ml. reagent chloroform and 14.7 g. of N-chlorosuccinimide (0.11 mole) was added in one portion. The mixture was heated under reflux for 3 hours. As no apparent reaction had taken place, two 1.0-g. portions of benzoyl peroxide was added at half-hour intervals. After heating the solution under reflux an additional 45 minutes, the mixture was

illuminated with a 1000-watt bulb for 20 minutes. No heat effect was noted. The mixture was cooled in an ice bath and the unchanged n-chlorosuccinimide recovered by suction filtration. The chloroform was removed at the water pump and the residue then distilled to recover 84-per-cent unreacted methyl crotonate. The small amount of pot residue gave a negative Beilstein test for halogen.

Stereochemistry of the Substituted Acrylic Acids.-- The trans nature of fumaric acid is too well known to require comment. The crotonic acid isomer that we used (m.p. 72°) has also been fairly convincingly shown to be trans,[37] by an argument that also supports the trans structural assignment for the γ,γ-dichlorocrotonic acid and the γ,γ,γ-trichlorocrotonic acids that we used. Backer and Beute[30] has given the evidence for the structure of trans β-chloro-propionic acid which includes its higher melting point, lower acidity and lower solubility. According to Shaw, the ultraviolet spectrum of solutions of β-acetylacrylic acid is like that of an α,β-unsaturated lactone showing that the compound must exist almost entirely as the pseudo acid.[11]



Except for the one we have referred to as cis, all of the nitro-substituted acrylic acids are probably trans. The trans compounds are more stable than the cis particularly when the group attached directly to the double bond is rather bulky as it is with the compounds we used. Even in the case of the smaller

(37) Cf. E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Publishing Company, Amsterdam, Vol I A, p 632.

chlorine atom it should be noted that the addition of hydrogen chloride to propiolic acid yields largely the trans β-chloroacrylic acid.[30] It seems likely that the addition of even larger molecules to propiolic acid and its derivatives would be even more likely to give trans substituted acrylic acids. In the case of the addition 2-nitropropane, where two products are obtained, Dr. Lloyd A. Kaplan has described to us the infrared evidence that the lower melting isomer, obtained in higher yield, is the trans compound.

Technique of Rate Determination.--The technique used in carrying out the rate determination is most easily described in terms of a representative example.[38]

A stock solution of the compound whose rate was to be determined was prepared by weighing out a known amount of the compound and transferring the material quantitatively to an appropriate volumetric flask. The material was dissolved in ca 80-90 per cent of the calculated amount of absolute ethanol and thermostatted at 30°C for at least one hour. In the meantime, a solution of diphenyldiazomethane of the prescribed concentration in absolute ethanol was also thermostatted along with a series of 25-ml low actinic volumetric flasks which served as mixing bottles for the acid and diphenyldiazomethane solutions. The ultraviolet spectrometer was turned on and allowed to reach equilibrium during the period in which the above solutions were thermostatted. Immediately before the start of the kinetic runs, the stock solution of the acidic substance was diluted to final volume with absolute ethanol at 30°C.

The mixing of the acidic stock solution and the diphenyldiazomethane stock solution was carried out as follows: The prescribed aliquot of

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(38) Cf. J. D. Roberts and W. T. Moreland, J. Am. Chem. Soc., 75, 2167 (1953).

diphenyldiazomethane stock solution was pipetted into the thermostatted mixing flasks, and if necessary, in order to obtain the diphenyldiazomethane and acid concentrations desired, a measured amount of absolute ethanol was added. This solution was further thermostatted for ca 5 minutes during which time a final adjustment of the ultraviolet spectrophotometer was made, using absolute ethanol as the blank solution. A measured aliquot of acidic stock solution was then added to the mixing bottle containing diphenyldiazomethane in absolute ethanol and the mixed solution was transferred immediately to the thermostatted cell of the instrument. The time lapse from the start of acid addition to the initial optical density reading varied from approximately 15 to 30 seconds, depending upon the aliquot of acidic component taken. The stopwatch was started upon taking the initial optical density reading. Additional readings were taken at selected time intervals throughout at least two half-lives of the reaction. A cell correction was then taken using absolute ethanol in the same cell that was used for the rate determination. A plot of the optical density readings taken at 525 mμ versus time (expressed in minutes), using semi-logarithmetic graph paper, optical density being plotted on the logarithmic scale, gave a straight line. The half-life of the reaction under these conditions was determined from the graph, and the second-order rate constant was calculated from the equation

$$k = \frac{(0.69315)(A)}{(B)(t\frac{1}{2})(C)}, \text{ where}$$

k = second-order rate constant.

A = total ml. of solution.

B = ml. of acidic component.

C = molarity acidic stock solution.

$t\frac{1}{2}$ = half-life of D.D.M. disappearance.

The numerical data obtained in the reaction of γ,γ,γ-trichlorocrotonic acid with diphenyldiazomethane in absolute ethanol at 30° are as follows.

A stock solution of acid was prepared by dissolving 0.9855 g. of γ,γ,γ-trichlorocrotonic acid in 50.00 ml. of absolute ethanol. A 2.00-ml. aliquot of about 0.035-M diphenyldiazomethane in ethanol was diluted with 5.00 ml. of ethanol, and 3.00 ml. of the stock solution of γ,γ,γ-trichlorocrotonic acid was added. Starting immediately after mixing the solutions, optical density readings were made at 525 mμ, with the results shown in Table V.

TABLE V

REACTION OF γ,γ,γ-TRICHLOROCROTONIC ACID
WITH DIPHENYLDIAZOMETHANE IN ETHANOL AT 30°

$[Cl_3CCH = CHCO_2H]_o$ = 0.0312 M; $[DDM]_o^a$ = 0.00566 M

Time (min.)	D[b]	Time (min.)	D[b]
0.00	0.538	5.00	.232
.50	.488	6.00	.196
1.00	.459	7.00	.158
2.00	.386	8.00	.137
3.00	.317	9.00	.120
4.00	.266	10.00	.107

[a] Diphenyldiazomethane concentration.

[b] Optical Density, corrected by adding a cell correction of 0.001.

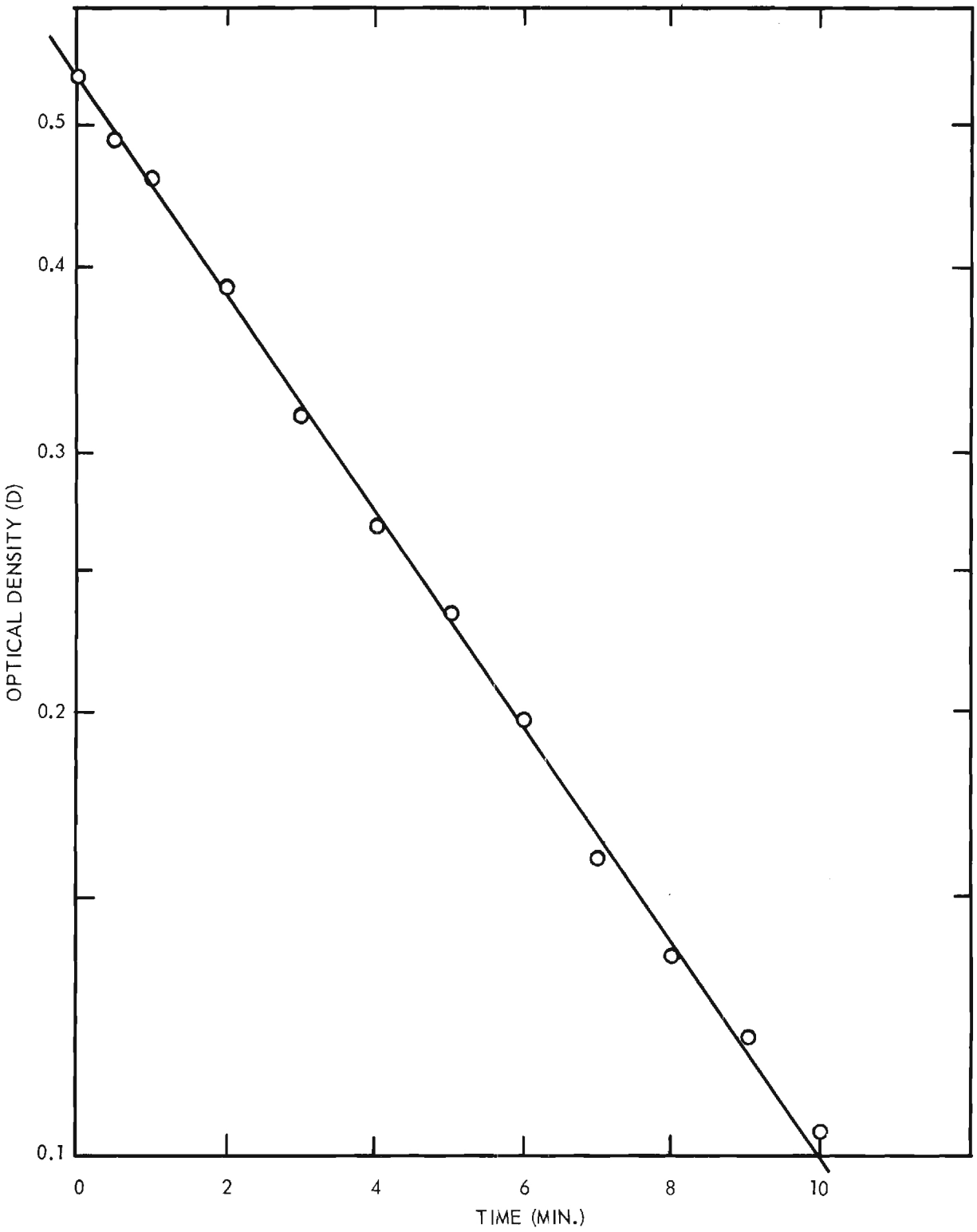

Figure 5. Reaction of γ,γ,γ-Trichlorocrotonic Acid with Diphenyldiazomethane in Absolute Ethanol at 30°.

In Fig. 5 the data of Table V are plotted. The plot of the logarithm of the optical density versus the time is seen to fall reasonably near a straight line. From this line k may be calculated to be 5.42 l./mole-min. In other runs values of 5.36 and 5.39 l./mole-min. were obtained.

A summary of all the kinetic runs made is given in Table VI.

TABLE VI

SUMMARY OF KINETIC RUNS ON THE REACTIONS OF ACIDIC COMPOUNDS (HA) WITH DIPHENYLDIAZOMETHANE IN ABSOLUTE ETHANOL AT 30°

HA	$[HA]_o$	$[D.D.M.]_o$	k^a
Benzoic Acid	.0899	.00650	1.01
Benzoic Acid	.0632	.00385	1.00
Benzoic Acid	.0674	.00527	1.03
Benzoic Acid	.0482	.00305	0.98
4,4,4-Trinitrobutyric Acid	.0506	.00217	3.80
4,4,4-Trinitrobutyric Acid	.0324	.00239	3.80
4,4,4-Trinitrobutyric Acid	.0725	.00416	3.68
4,4-Dinitropentanoic Acid	.0300	.00267	2.03
4,4-Dinitropentanoic Acid	.0672	.00502	2.05
4,4-Dinitropentanoic Acid	.0616	.00374	2.02
4,4-Dinitrohexenoic Acid	.0143	.00088	13.80
4,4-Dinitrohexenoic Acid	.0147	.00130	12.96
4,4-Dinitrohexenoic Acid	.0157	.00257	12.24
trans-4-Methyl-4-nitropentenoic Acid	.0218	.00118	2.48
trans-4-Methyl-4-nitropentenoic Acid	.0382	.00412	2.54

(continued)

TABLE VI (continued)

SUMMARY OF KINETIC RUNS ON THE REACTIONS OF ACIDIC COMPOUNDS (HA) WITH DIPHENYLDIAZOMETHANE IN ABSOLUTE ETHANOL AT 30°

HA	$[HA]_o$	$[D.D.M.]_o$	k^a
trans-4-Methyl-4-nitropentenoic Acid	.0286	.00145	2.44
β-Nitroacrylic Acid	.0229	.00126	22.2
β-Nitroacrylic Acid	.0357	.00123	21.4
cis-4-Methyl-4-nitropentenoic Acid	.0301	.00122	3.54
cis-4-Methyl-4-nitropentenoic Acid	.0421	.00269	3.41
Saccharin	.0194	.00536	18.4
Saccharin	.0194	.00891	18.4
Saccharin	.0138	.00525	20.0
Saccharin	.0323	.00291	19.7
γ,γ,γ-Trinitrocrotonic Acid	.0178	.00231	25.9
γ,γ,γ-Trinitrocrotonic Acid	.0134	.00350	24.2
γ,γ,γ-Trinitrocrotonic Acid	.0201	.00327	26.7
γ,γ,γ-Trinitrocrotonic Acid	.0089	.00592	26.3
Fumaric Acid	.0522	.00587	6.89
Fumaric Acid	.0298	.00572	6.50
Fumaric Acid	.0348	.00275	6.74
Crotonic Acid	.0835	.00446	0.594
Crotonic Acid	.0752	.00636	0.624
Crotonic Acid	.0556	.00298	0.612
γ,γ,γ-Trichlorocrotonic Acid	.0578	.00433	5.39

(continued)

TABLE VI (concluded)

SUMMARY OF KINETIC RUNS ON THE REACTIONS OF ACIDIC COMPOUNDS (HA) WITH DIPHENYLDIAZOMETHANE IN ABSOLUTE ETHANOL AT 30°

HA	$[HA]_o$	$[D.D.M.]_o$	k^a
γ,γ,γ-Trichlorocrotonic Acid	.0473	.00198	5.36
γ,γ,γ-Trichlorocrotonic Acid	.0312	.00566	5.42
γ,γ-Dichlorocrotonic Acid	.0538	.00465	2.40
γ,γ-Dichlorocrotonic Acid	.0440	.00269	2.35
γ,γ-Dichlorocrotonic Acid	.0291	.00598	2.32
trans-β-Chloroacrylic Acid	.0498	.00166	2.44
trans-β-Chloroacrylic Acid	.0580	.00507	2.49
trans-β-Chloroacrylic Acid	.0475	.00259	2.51
trans-β-Acetylacrylic Acid	.0626	.00155	4.06
trans-β-Acetylacrylic Acid	.0940	.00148	4.03
trans-β-Acetylacrylic Acid	.0188	.00198	3.99
Acrylic Acid	.0881	.00422	1.28
Acrylic Acid	.0353	.00306	1.25
Acrylic Acid	.0605	.00366	1.29
4,4-Dinitropentenoic Acid	.0295	.00082	11.43
4,4-Dinitropentenoic Acid	.0303	.00126	11.10
4,4-Dinitropentenoic Acid	.0323	.00224	11.98

[a] In liters/moles · minutes.

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